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Assessment of Perchlorate Releases in Launch Operations III

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14. ABSTRACT

A method for predicting potential perchlorate releases from accidental launch failures has been developed for use in planning and managing launch activities where solid rocket motors are used. The method is also applicable to assessing location and quantity of perchlorate release in the event that a launch failure has already occurred. A representative hypothetical case study is presented to illustrate time scales for potential perchlorate release into bodies of water under different conditions of temperature and salinity. The report also contains an analysis of water samples (for metals and other contaminants) in which solid propellant samples were immersed for 11 months.

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1. Introduction

1.1 Background

In earlier reports we have described the results of laboratory studies that determined rates of perchlorate release from several different perchlorate-containing solid rocket propellants, under various temperature and salinity conditions.[1,2] The release rates were reported as diffusion coefficients ranging from 3.6×10^{-12} to 1.1×10^{-13} m^2s^{-1}.

In this current report, we have included an Appendix containing the results of comprehensive analyses of water samples previously used in the earlier chemical kinetics experiments. The water was analyzed for other contaminants such as metals or organic substances, which may have leached from the propellant samples along with the ClO_4^-.

A method for determining solid propellant impact probability distributions and expected solid propellant weight distributions for potential launch failures was also presented in the earlier reports. Case studies for solid propellant-containing vehicles launched from VAFB and CCAFS were also analyzed.

1.2 Implementation of the Perchlorate Release Analysis Process

In this report, we present a method for predicting perchlorate release in the event of a launch failure that incorporates both the previously determined diffusion coefficients for perchlorate release from solid propellants and a quantitative debris prediction model. The methodology quantifies the expected amount of perchlorate released in the event of a failure for a particular vehicle and particular flight azimuth over a particular launch site location. It considers burning of the propellant as it falls through the atmosphere. In the aftermath of a launch failure, the method can be used to determine where clean-up or other mitigation measures should be applied.

The steps used in the proposed process for the assessment of potential perchlorate releases from a launch failure are outlined in Section 2. In Section 3, we present a hypothetical launch failure case study to illustrate how the amount of perchlorate released can be determined for a typical trajectory over a typical launch site. Examples of perchlorate release scenarios for various sizes of propellant fragments exposed to water are illustrated as a function of time.

The method described can also be used for launch planning prior to selecting trajectories for a particular vehicle. When used with failure probabilities, this method provides a way to assess and manage the risks associated with potential perchlorate releases from potential launch failures. Typically such information is needed in environmental, safety, and health analyses during the planning phases for a launch system.

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2. A Stepwise Approach to the Assessment of Accidental Perchlorate Release from Launch Failure

Table 2.1 summarizes our suggested stepwise approach to quantifying impacts from accidental perchlorate releases in the event of a launch failure. Before presenting a representative case study using this approach in Section 3, a brief description of the steps is given.

Table 2.1. Suggested Steps in the Quantification of Accidental Perchlorate Release From Launch Failures

	Assessment Steps	Comments
1.	Establish launch vehicle and mission information - solid-propellant mass - composition of propellant - burn rate - trajectory	Use real data for the mission of interest wherever possible.
2.	Establish failure probabilities.	Failure probabilities are used for predictions if the risk assessment is performed prior to launch. For the assessment of a launch failure that has already occurred, the failure probability is equal to one.
3.	Determine or select point(s) of failure on trajectory. - time - position - velocity	If assessing a failure that has occurred, this point will be known. For predictions, multiple possible failure points along a trajectory may be selected. These can be used to compare the relative risks of failures at different times.
4.	Obtain a debris model for the launch vehicle configuration(s).	Sources can include the launch vehicle contractor for the mission or a safety representative. (Previous reports have referenced the ACTA Debris model[1,2]).
5.	Determine size and weight of pieces of unburned propellant at time of surface impact.	Our current model has a lower size limit of 7 lb at the time of failure. The fragment size at impact depends on the burn rate and time to surface impact.
6.	Determine distribution pattern of pieces on surface grid (or map of launch site). The number of particles per each bin size is also determined.	The areas of impact are bounded by cross-range and down-range distances. For an actual case at a specified range, the geographical coordinates (longitude and longitude) are determined.
7.	Establish characteristics of the surface environment where the propellant fragments landed. - soil type - fresh or salt water - temperature - wetlands - other	Specific to each particular launch site, trajectory, and other factors such as season and weather conditions.
8.	Determine amount of perchlorate ion released from propellant fragments into the environment as a function of time.	Factors such as volume(s) of impacted water bodies, flow conditions, and temperature are all relevant to this step. However, simplifying assumptions may need to be made if all of the actual data are not available.
9.	Compare instantaneous and steady-state concentrations of perchlorate to levels that affect biological/environmental receptors.	This requires data on toxicity, uptake, and persistence of ClO_4^- in the environment and species of concern. These issues are not addressed in this report.
10.	Make informed management decisions about launch.	Requires integration of all available information.

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3. Representative Study of Perchlorate Release from a Launch Failure

To illustrate our method for the assessment of perchlorate release from a failed launch with solid rocket motors, we have created a representative, vehicle and scenario. For this example, we use a two-stage solid-propellant vehicle, launched with a typical trajectory from a generic range. To complete the scenario, a representative environment surrounding the launch site was created, including areas covered by soil, a fresh water lake, and a body of salt water (ocean). Terrain factors such as altitude are not considered.

Following the steps outlined in Table 2.1, the case study is presented here.

3.1 Establish Launch Vehicle and Mission Information

For this example case study, a small, two-stage, solid-propellant launch vehicle was chosen. It has a gross liftoff weight of 150,000 lb. The total amount of solid propellant in the vehicle is 128,950 lb. We assume the propellant is hydroxyl-terminated polybutadiene propellant (HTPB) containing 69% ammonium perchlorate by weight. The density of the propellant is assumed to be 1.80 g/cm^3.

The vehicle rises vertically for the first 4 s, then gradually pitches into an easterly flight azimuth and ascends to a low earth orbit. The initial 30 s of flight is the only phase of concern for this case because after that the vehicle is well downrange of the launch area and over open ocean.

A representative launch site with a coastal location is depicted in Figure 3.1. The site includes a small, freshwater lake that is 0.3 mi. from the launch pad. The launch site and nominal trajectory ground trace are shown in Figure 3.1

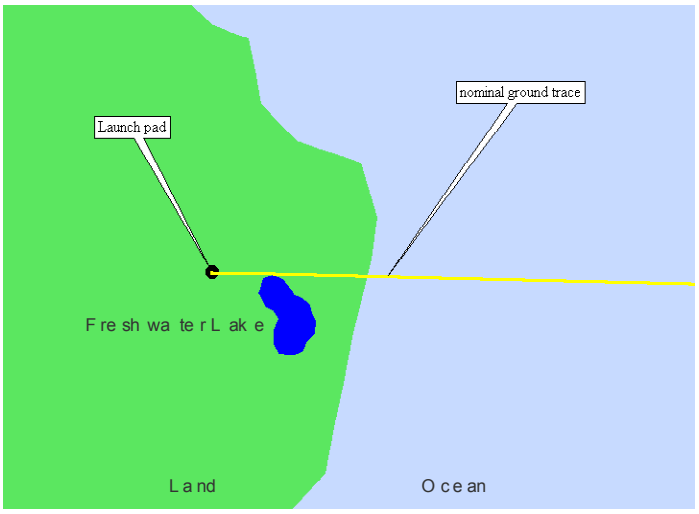

Figure 3.1. Representative launch site and trajectory ground trace.

3.2 Establish Failure Probabilities

For this particular case, we are assuming that a launch failure has occurred; therefore, the failure probability is equal to one. See next section for more details.

3.3 Determine or Select Point of Failure

Since we are modeling a case where a launch failure is assumed to have occurred, the time and altitude along the trajectory are known. For this case, we assume a failure occurred at 15 s after liftoff while on an otherwise normal ascent. Such an accident might occur if the vehicle experienced a sudden loss of control that triggered the auto-destruct system. For comparison, another example case was modeled with a launch failure at 25 s after liftoff. Data for these two cases are presented in Tables 3.1 and 3.2, respectively. These are discussed further in Subsection 3.5.

3.4 Obtain a Debris Model

A typical solid-propellant debris model was constructed based on similarity to models that are currently used to support range safety analysis.[3]

3.5 Determine Size and Weight of Unburned Propellant Fragments

The solid-propellant fragments are divided into categories (or debris classes) determined by ballistic coefficient. For this hypothetical case study, a number of debris classes, calculated for a 15-s launch failure are given in Table 3.1. Likewise, debris classes for a 25-s failure are listed in Table 3.2. The ballistic coefficient is a measure of how a free-falling object is affected by aerodynamic drag. In general, for this type of debris model, the larger size fragments have higher ballistic coefficients and are fewer in number. Whereas, there are hundreds of smaller size fragments that have lower ballistic coefficients. The model assumes that all first-stage propellant pieces continue burning during descent to ground impact at an average burn rate of 0.1 in./s (from outer surface inward). Trajectory simulations were run to estimate debris impact times. Tables 3.1 and 3.2 define the selected debris model. The later destruct time of 25 s reflects the additional burning of propellant both on ascent and descent, with the exception of the largest piece, which is the intact second stage.

Table 3.1. Solid Propellant Debris Model for Example Case—Destruct at 15 s

Ballistic Coefficient (psf)	Imparted Velocity (fps)	# of Fragments	Weight of Fragments at Destruct (lb)	Weight of Fragments at Impact (lb)
153	1	1	21711.0	21711.0
881	103	1	2890.0	2183.1
800	103	2	2120.0	1546.9
554	107	6	1389.0	1008.7
471	117	13	856.0	585.1
391	130	33	490.0	307.8
312	147	79	249.0	137.7
234	172	183	105.0	46.8
159	211	321	33.0	9.3
95	277	181	7.0	0.6

Table 3.2. Solid Propellant Debris Model for Example Case—Destruct at 25 s

Ballistic Coefficient (psf)	Imparted Velocity (fps)	# of Fragments	Weight of Fragments at Destruct (lb)	Weight of Fragments at Impact (lb)
153	1	1	21711.0	21711.0
561	131	2	2163.0	1176.4
494	131	4	1381.0	654.7
329	136	10	868.0	406.5
272	151	28	490.0	190.2
216	171	69	247.0	70.5
162	199	171	104.0	15.8
110	245	312	33.0	1.0

The size of the fragments influences the release rate because if, for a given propellant mass, there are many small fragments, the perchlorate will be released more quickly, leading to higher initial concentrations, but then the overall time (years) until all of the perchlorate is released, will be shortened. Breakup of unretrieved fragments over time as a result of environmental factors may occur on land or in waters. This would increase the perchlorate release rate but cannot be readily predicted.

3.6 Determine Distribution of Propellant on Surface Grid

In the preceding report,[2] a methodology was presented to calculate the expected weight $E[W]_i$ of solid propellant landing in a particular region. It can be summarized by the following equation.

$$E\left[W\right]_i = \Delta t \times P_{Frate} \times n_{frag} \times W_{frag} \int_{x_i-\frac{\Delta x_i}{2}}^{x_i+\frac{\Delta x_i}{2}} \int_{y_i-\frac{\Delta y_i}{2}}^{y_i-\frac{\Delta y_i}{2}} f(x,y)\,dy\,dx$$

P_{Frate} - the vehicle failure rate
Δt - the dwell time over the impact region of concern
$f(x,y)$ - the bivariate impact probability density function
x_i - the downrange distance to the center of the i^{th} area
y_i - the crossrange distance to the center of the i^{th} area
Δx_i - the downrange length of the i^{th} area
Δy_i - the crossrange width of the i^{th} area
n_{frag} - number of fragments
W_{frag} - average weight of each fragment

For this case study, the dwell time multiplied by the failure rate is set equal to one ($P_{failure} = 1$), which meets the aforementioned assumption that a failure has occurred.

To estimate the probability density function, a Monte Carlo trajectory simulation technique was utilized to determine the probability of impact for each debris class (i.e., ballistic coefficient) for the three areas: lake, ocean, and land. Velocity imparted to the debris due to the vehicle destruct is input in a random direction for each Monte Carlo sample trajectory. Expected weights were calculated, and results from the analysis are given in Tables 3.3 and 3.4. The geographic distribution of perchlorate fragments is shown in Figures 3.2 and 3.3.

Table 3.3. Expected Weight for Solid Propellant Impacts—Destruct at 15 s

Ballistic Coefficient (psf)	# of Fragments	Weight of Fragments (lb)	Expected Weight in Lake (lb)	Expected Weight in Lake (lb)	Expected Weight on Land (lb)
153	1	21711.0	0	0	21711.0
881	1	2183.1	109.2	0	2041.2
800	2	1546.9	154.7	0	2892.7
554	6	1008.7	308.7	0	5663.6
471	13	585.1	403.1	0	7070.1
391	33	307.8	353.5	18.3	9678.0
312	79	137.7	224.1	39.2	10519.3
234	183	46.8	182.4	31.1	8268.2
159	321	9.3	65.7	10.9	2877.4
95	181	0.6	3.1	0	103.8
Total	820		1804.5	99.5	70825.3

Table 3.4. Expected Weight for Solid Propellant Impacts—Destruct at 25 s

Ballistic Coefficient (psf)	# of Fragments	Weight of Fragments (lb)	Expected Weight in Lake (lb)	Expected Weight in Ocean (lb)	Expected Weight on Land (lb)
153	1	21711.0	0	21711.0	0
561	2	1176.4	0	2265.7	87.1
494	4	654.7	0	2493.0	125.7
329	10	406.5	4.1	3825.1	235.8
272	28	190.2	31.9	4749.9	536.2
216	69	70.5	53.5	4095.5	701.9
162	171	15.8	36.8	2043.4	613.3
110	312	1.0	5.1	208.9	96.9
Total	597		131.4	41392.4	2396.8

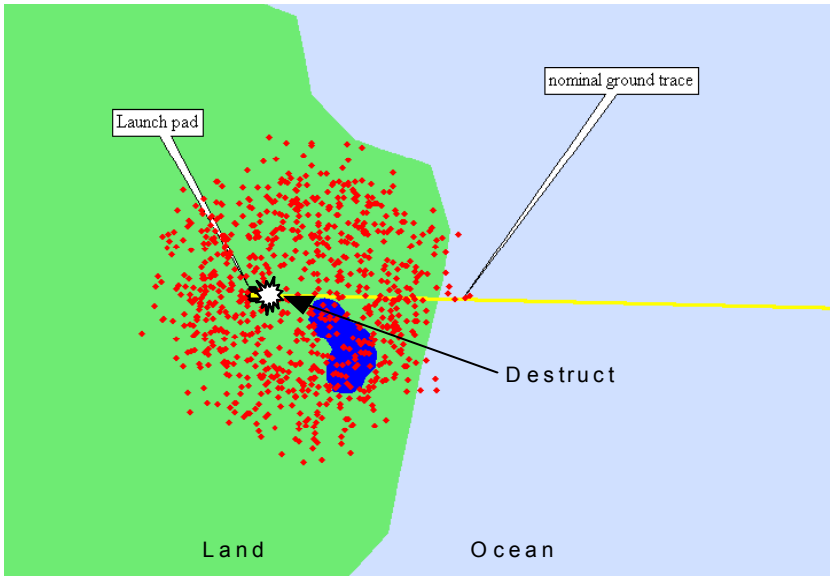

Figure 3.2. Solid propellant fragment impact locations for a vehicle destruct at 15 s.

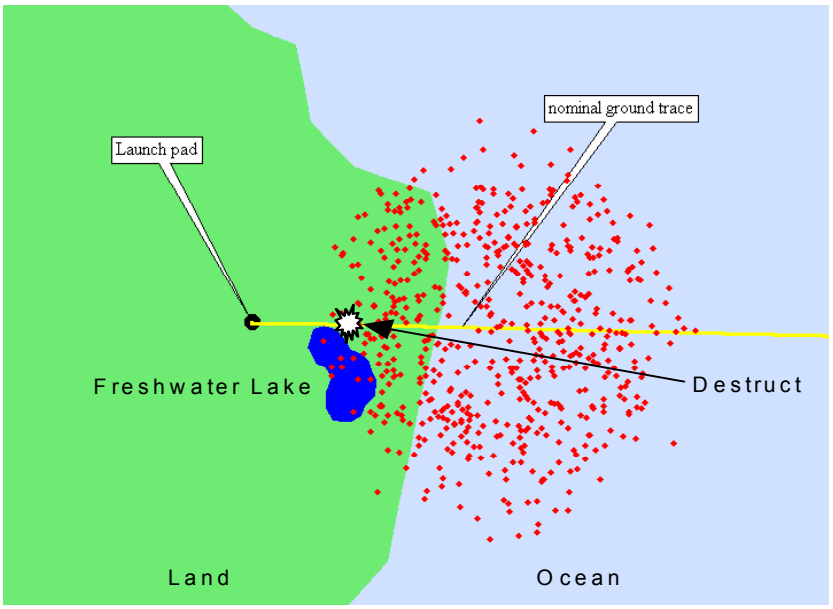

Figure 3.3. Solid propellant fragment impact locations for a vehicle destruct at 25 s.

3.7 Establishing Characteristics of Surface Environment

Solid HTPB propellant fragments impacting land may release perchlorate. An exposed propellant fragment would be subject to rain that could quickly dissolve any exposed perchlorate crystals. The presence of water from rain, fog, or soil moisture would allow diffusion of perchlorate to the surface of the fragment. Wind erosion and solar degradation of the binder may contribute to the fragment breakup, exposing additional surfaces to the environment. A buried fragment may be subject to soil moisture and seepage from surface waters, allowing the diffusion of perchlorate ion from the fragment. These mechanisms cannot be readily quantified but should be considered in perchlorate management decisions.

Solid HTPB propellant fragments impacting in water will release perchlorate. The amount of perchlorate released from submerged solid propellant into waters over a given time period can be estimated based upon the propellant perchlorate diffusion rate for the propellant type, the water characteristics, the particle size distribution, and the fraction of the propellant debris field that falls into the water. Propellant perchlorate diffusion rates in salt and fresh water for various solid propellants are known, and sufficient data exists to extrapolate rates for the water temperature.[2] Propellant perchlorate diffusion rates for other solid propellants have been measured in the laboratory as well.

For solid propellant deposited in water, the factor limiting perchlorate release is the perchlorate diffusion rate out of the solid propellant, 3.6×10^{-12} to $1.1 \times 10^{-13} m^2 s^{-1}$.[2] Once the perchlorate ion is released from the solid propellant to the surrounding water, it diffuses at the faster perchlorate in water diffusion rate, $1.79 \times 10^{-5} m^2 s^{-1}$ at 25°C.[4] In marine sediments, the diffusion coefficients of strong electrolytes is on the order of $10^{-10} m^2 s^{-1}$.[5]

Water currents may transport the perchlorate ion rapidly. The water current transport of released perchlorate ion will be similar to that of other dissolved salts in the water. Near-bed ocean currents are strongly affected by local topography and difficult to predict from measurements made above. The sub-tidal near-bed water currents of California have been reported as 0.2 to 15 cm/s depending on location. Currents at a depth of 250 m can be 30 cm/s or more. On the outer shelf, current speeds near the bed can exceed 45 cm/s. Ocean currents may or may not show seasonal or temporal patterns.[6] These rates are summarized in Table 3.5.

Table 3.5 summarizes transport rates. For this table, diffusion coefficients and the Einstein-Smoluchowski relationship[2] have been used to calculate the root-mean-square distance, in meters, traveled by a diffusing perchlorate ion in one second. For comparison, water current velocities in meters per second are shown. It can be seen that the transport by diffusion is much slower than the velocity of water currents and that the slowest transport rate seen is for the propellants.

The release rate of perchlorate into water is dependant on the water temperature. In cases where the water immediately surrounding the propellant freezes, the release rate would be expected to become very slow. Freezing may not occur at 0°C since the salts in the water and material coming from the propellant will cause freezing point depression. In cases where there are wide seasonal fluctuations, accuracy in calculating the expected release may be improved by considering seasons separately.

Table 3.5. Summary of Transport Rates

Root mean square distance (m) traveled by a diffusing perchlorate ion in one second	
Propellants	2.7E-06 to 4.7E-07
Distilled water	6.0E-05
Marine sediments	~1.4E-05
Velocity of water currents (ms^{-1})	
Sub-Tidal near bed ocean currents	2.0E-03 to 1.5E-01
Outer shelf near bed ocean currents	4.5E-01

3.8 Determining the Amount of Perchlorate Released into the Environment as a Function of Time

Determining the perchlorate release requires data on the propellant fragment size, the propellant physical characteristics, and the water temperature and salinity conditions. The release rate from different sized fragments can be weighted by the number of fragments in the debris class and combined to get an overall release rate.

Relevant propellant physical properties of four tpes of solid propellants are shown in Table 3.6. The percent ammonium perchlorate was provided by the propellant manufacturer. The density values were obtained by measuring the weight and volume of the propellant specimens used to determine the diffusion coefficients.[2] The propellants described here were used in earlier chemical kinetics studies.[2] The four types of propellants are characterized by the binder in each formulation, hydroxyl-terminated polybutadiene (HTPB), carboxy-terminated polybutadiene (CTPB), polybutadiene acrylic acid acrylonitrite (PBAN), and polyurethane (PU). These propellants are also described in the Appendix to this report.

Table 3.6. Physical Properties of Solid Propellants

Propellant Type	Weight % NH_4ClO_4	Density (g/cm^3)
HTPB	69.0	1.80
CTPB	73.0	1.75
PBAN	69.8	1.74
PU	65.4	1.55

The perchlorate release from a fragment of propellant submerged in water is related to the size of the fragment, the perchlorate content, the binder type, the water salinity, and the temperature conditions. Fragment shapes are not readily predictable; so in calculating perchlorate release, a simplifying assumption is made that the fragments are spherical. The weight and propellant density are used to compute the spherical fragment diameter.

The diffusion coefficient, reflecting the propellant type, water type, and temperature, is used to calculate the characteristic diffusion time and the expected perchlorate release. Diffusion coefficients have been measured for several propellants.[2] Tables 3.7 and 3.8 show the diffusion coefficients for HTPB, CTPB, PBAN, and PU propellants in pure water and in simulated seawater. These table values were calculated by applying the Arrhenius equation for each propellant type at the indicated temperature and salinity. The terms were obtained from laboratory measurements of diffusion coefficients made at 5°C, 20°C and 29°C.[2] The values in these tables are interpolated between measured temperature conditions and extrapolated beyond the measured temperature conditions.

Table 3.7. Diffusion Coefficients in Pure Water at Various Temperatures for Solid Propellants (m^2s^{-1})

°C	HTPB	CTPB	PBAN	PU
35	2.22E-12	1.84E-12	2.10E-12	4.39E-12
34	2.10E-12	1.76E-12	2.03E-12	4.25E-12
33	2.00E-12	1.68E-12	1.97E-12	4.11E-12
32	1.90E-12	1.61E-12	1.90E-12	3.97E-12
31	1.80E-12	1.54E-12	1.84E-12	3.84E-12
30	1.71E-12	1.47E-12	1.77E-12	3.71E-12
29	1.62E-12	1.40E-12	1.71E-12	3.58E-12
28	1.53E-12	1.34E-12	1.66E-12	3.46E-12
27	1.45E-12	1.28E-12	1.60E-12	3.34E-12
26	1.37E-12	1.22E-12	1.54E-12	3.22E-12
25	1.30E-12	1.16E-12	1.49E-12	3.11E-12
24	1.23E-12	1.11E-12	1.44E-12	3.00E-12
23	1.16E-12	1.06E-12	1.39E-12	2.89E-12
22	1.10E-12	1.01E-12	1.34E-12	2.79E-12
21	1.04E-12	9.61E-13	1.29E-12	2.69E-12
20	9.83E-13	9.15E-13	1.24E-12	2.59E-12
19	9.28E-13	8.71E-13	1.20E-12	2.50E-12
18	8.76E-13	8.29E-13	1.15E-12	2.41E-12
17	8.27E-13	7.89E-13	1.11E-12	2.32E-12
16	7.80E-13	7.50E-13	1.07E-12	2.23E-12
15	7.35E-13	7.13E-13	1.03E-12	2.15E-12

°C	HTPB	CTPB	PBAN	PU
14	6.93E-13	6.78E-13	9.91E-13	2.07E-12
13	6.53E-13	6.44E-13	9.54E-13	1.99E-12
12	6.15E-13	6.12E-13	9.17E-13	1.92E-12
11	5.79E-13	5.81E-13	8.82E-13	1.84E-12
10	5.44E-13	5.51E-13	8.48E-13	1.77E-12
9	5.12E-13	5.23E-13	8.15E-13	1.70E-12
8	4.81E-13	4.96E-13	7.83E-13	1.63E-12
7	4.52E-13	4.70E-13	7.52E-13	1.57E-12
6	4.25E-13	4.45E-13	7.22E-13	1.51E-12
5	3.99E-13	4.22E-13	6.94E-13	1.45E-12
4	3.74E-13	3.99E-13	6.66E-13	1.39E-12
3	3.51E-13	3.78E-13	6.39E-13	1.33E-12
2	3.29E-13	3.58E-13	6.13E-13	1.28E-12

Table 3.8. Diffusion Coefficients in Simulated Seawater at Various Temperatures for Solid Propellants (m^2s^{-1})

°C	HTPB	CTPB	PBAN	PU
35	1.94E-12	1.27E-12	1.76E-12	2.33E-12
34	1.83E-12	1.19E-12	1.68E-12	2.24E-12
33	1.72E-12	1.11E-12	1.60E-12	2.15E-12
32	1.62E-12	1.04E-12	1.53E-12	2.06E-12
31	1.53E-12	9.72E-13	1.46E-12	1.98E-12
30	1.44E-12	9.09E-13	1.39E-12	1.90E-12
29	1.35E-12	8.49E-13	1.33E-12	1.82E-12
28	1.27E-12	7.93E-13	1.26E-12	1.74E-12
27	1.20E-12	7.41E-13	1.20E-12	1.67E-12
26	1.13E-12	6.91E-13	1.15E-12	1.60E-12
25	1.06E-12	6.45E-13	1.09E-12	1.53E-12
24	9.95E-13	6.01E-13	1.04E-12	1.47E-12
23	9.34E-13	5.60E-13	9.90E-13	1.41E-12
22	8.76E-13	5.22E-13	9.41E-13	1.35E-12
21	8.22E-13	4.86E-13	8.95E-13	1.29E-12
20	7.71E-13	4.52E-13	8.51E-13	1.23E-12
19	7.23E-13	4.21E-13	8.09E-13	1.18E-12
18	6.77E-13	3.91E-13	7.68E-13	1.12E-12
17	6.34E-13	3.63E-13	7.29E-13	1.07E-12
16	5.93E-13	3.37E-13	6.92E-13	1.03E-12
15	5.55E-13	3.13E-13	6.57E-13	9.80E-13
14	5.19E-13	2.91E-13	6.23E-13	9.35E-13
13	4.85E-13	2.69E-13	5.91E-13	8.92E-13
12	4.54E-13	2.50E-13	5.60E-13	8.51E-13
11	4.24E-13	2.31E-13	5.31E-13	8.12E-13
10	3.95E-13	2.14E-13	5.03E-13	7.74E-13
9	3.69E-13	1.98E-13	4.76E-13	7.37E-13
8	3.44E-13	1.83E-13	4.50E-13	7.02E-13
7	3.21E-13	1.69E-13	4.26E-13	6.69E-13

°C	HTPB	CTPB	PBAN	PU
6	2.99E-13	1.56E-13	4.03E-13	6.37E-13
5	2.78E-13	1.44E-13	3.81E-13	6.06E-13
4	2.59E-13	1.33E-13	3.60E-13	5.76E-13
3	2.41E-13	1.23E-13	3.40E-13	5.48E-13
2	2.24E-13	1.13E-13	3.21E-13	5.21E-13

The characteristic diffusion time for a given fragment size is calculated using the diffusion coefficient. This characteristic diffusion time corresponds to the 1/e time, the time it takes for approximately 63.2% of the perchlorate to be released. Fitting this amount as a linear function of the square root of the characteristic diffusion time provides the release of perchlorate at various times.[2]

Table 3.9 shows an example of the size dependence of the solid propellant fragments on the expected time for perchlorate to be released. The table illustrates that for HTPB propellant in 20°C fresh water, it is expected that a 0.01 lb (4.5 g) fragment would cease to be a source of perchlorate after 9 months, while a 100 lb fragment would be expected to take 346 years to be depleted of perchlorate.

In summary, the total amount of perchlorate released into water depends on the propellant mass, the fragment weight, and number of fragments deposited in the water. The debris model provides the total number of fragments in various ballistic coefficient categories. The impact probability distribution model is used to predict the number of fragments landing in water.

Table 3.9. Perchlorate Release Time from HTPB 69% by weight Ammonium Perchlorate in 20°C Fresh Water

Propellant Fragment Weight (lb)	Extrapolated Time to Release All Perchlorate (Years)
0.01	0.75
0.10	3.5
1	16
2	25
5	47
10	75
25	137
55	232
100	346

3.8.1 Perchlorate Release Probability Calculation

In calculating perchlorate release, each debris class must be considered separately because the release rates are dependent on fragment size. The probability of impact for each debris class is used in calculating the total mass impacting the area of interest. Releases for each debris class are calculated separately and summed to give the total probable release expected over various time periods commencing from the impact. For the calculations in this report, it is assumed that the propellant is HTPB containing 69% ammonium perchlorate and the water temperature is 10°C. These calculations represent 100% launch failure and no cleanup effort, except in one case that considers fragment retrieval.

Impact Probability Distribution and Debris Model results were used to obtain probabilities of each debris class impacting the region of interest. The release probabilities from 15-s and 25-s vehicle destructs are calculated for two regions of interest, a fresh water lake and the ocean.

The debris dispersion modeling predicts that with destruct at 15 s, the probable amount of propellant released into the freshwater lake would be 1805 lb. The probable perchlorate release is calculated for each debris class given in the model. In Table 3.10, the sum is the probable cumulative perchlorate release in pounds during various time periods (in years) commencing from the impact time. This probable cumulative perchlorate release is shown graphically in Figure 3.4. A dashed line on the chart shows the total perchlorate present in the expected mass of propellant deposited in the region of interest at the time of impact. This is the upper bound for the cumulative perchlorate release for

Table 3.10. Probability Calculation of Cumulative Perchlorate Release into Fresh Water Lake from 15-s Launch Destruct; 1805 lb Propellant Enters Water

Debris Class	Expected cumulative pounds of perchlorate (ClO_4^-) released during various time spans (years)						
	1	2	5	10	20	30	50
21711	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2183	1.0	1.5	2.3	3.3	4.6	5.6	7.3
1547	1.6	2.3	3.7	5.2	7.3	9.0	11.6
1009	3.8	5.3	8.4	11.9	16.9	20.7	26.7
585	5.9	8.4	13.2	18.7	26.4	32.4	41.8
308	6.4	9.1	14.3	20.3	28.7	35.1	45.4
138	5.3	7.5	11.9	16.8	23.8	29.1	37.6
47	6.2	8.8	13.9	19.6	27.7	34.0	43.9
9.3	3.8	5.4	8.6	12.1	17.1	21.0	27.1
0.6	0.5	0.6	1.0	1.4	1.8	1.8	1.8
Sum	**34.6**	**48.9**	**77.3**	**109.3**	**154.4**	**188.7**	**243.1**

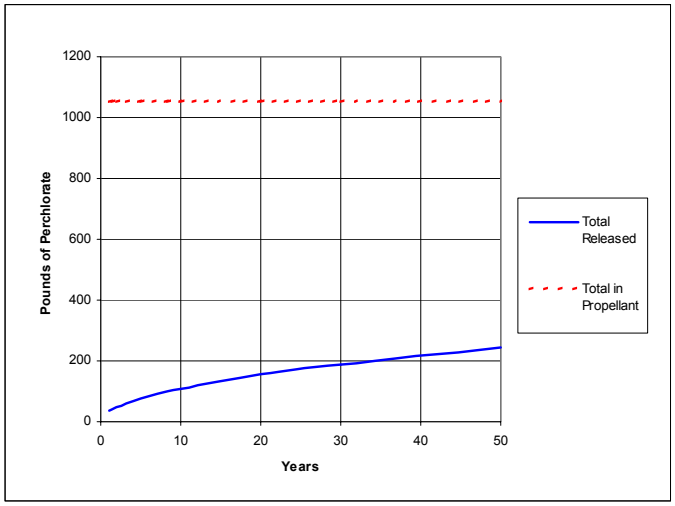

Figure 3.4. Probable cumulative perchlorate release into fresh water lake for 15-s launch destruct; 1805 lb propellant entering water.

this region of interest. Table 3.11 shows the same case expressed with probable mass of perchlorate release calculated for various 12-month periods following the incident. Figure 3.5 graphically shows how the annual release declines rapidly in early years but persists at lower levels for many years. The type of data provided in this table can provide input for perchlorate management decision-making. For example, the use of biological remediation in the event of long-term perchlorate releases may be considered in clean-up options if small fragments were to remain after initial retrieval effforts.

Table 3.11. Probability Calculation of Perchlorate Release into Fresh Water Lake from 15-s Launch Destruct; 1805 lb Propellant Enter Water, for Selected Years

Debris Class	Expected pounds of perchlorate (ClO_4^-) released during a given year						
	1	2	5	10	20	30	50
21711	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2183	1.0	0.4	0.2	0.2	0.1	0.1	0.1
1547	1.6	0.7	0.4	0.3	0.2	0.2	0.1
1009	3.8	1.6	0.9	0.6	0.4	0.3	0.3
585	5.9	2.4	1.4	1.0	0.7	0.5	0.4
308	6.4	2.7	1.5	1.0	0.7	0.6	0.5
138	5.3	2.2	1.3	0.9	0.6	0.5	0.4
47	6.2	2.6	1.5	1.0	0.7	0.6	0.4
9.3	3.8	1.6	0.9	0.6	0.4	0.4	0.3
0.6	0.5	0.2	0.1	0.1	0.0	0.0	0.0
Sum	**34.6**	**14.3**	**8.2**	**5.6**	**3.9**	**3.1**	**2.4**

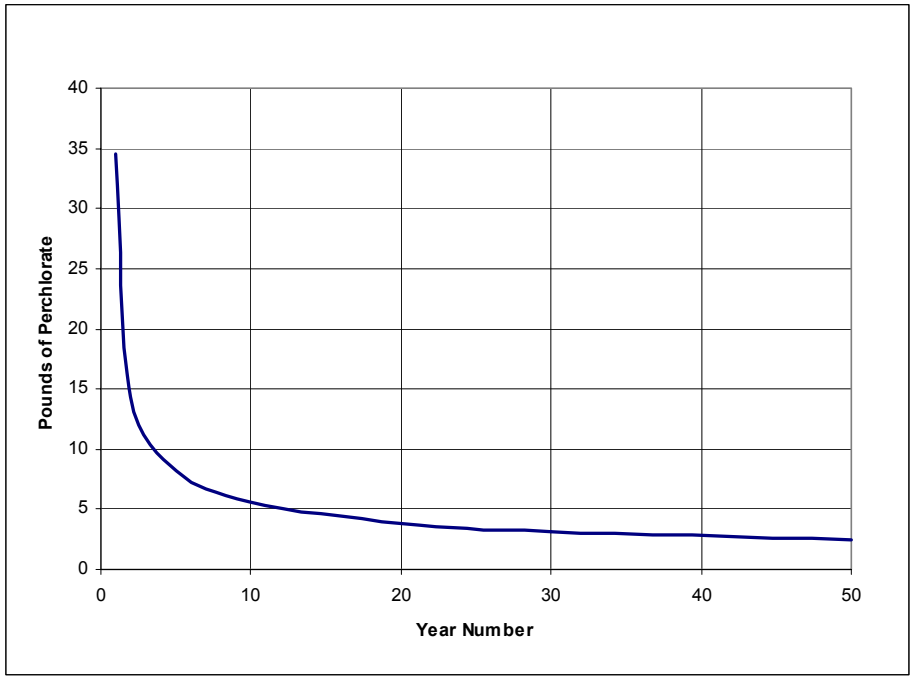

Figure 3.5. Expected perchlorate release into fresh water lake from 15-s launch destruct; 1805 lb propellant entering water, for selected years.

The debris dispersion modeling predicts that with destruct at 25 s, 131 lb of propellant would enter the lake. In Table 3.12, the sum is the probable cumulative perchlorate release in pounds during various time periods (in years) commencing from the impact time. This probable cumulative perchlorate release is shown graphically in Figure 3.6. Table 3.13 and Figure 3.7 show the same case expressed with probable mass of perchlorate release calculated for various 12-month periods following the incident.

Table 3.12. Probability Calculation of Cumulative Perchlorate Release into Fresh Water Lake for 25-s Launch Destruct; 131 lb Propellant Enters Water

Debris Class	Expected cumulative pounds of perchlorate (ClO_4^-) released during various time spans (years)						
	1	2	5	10	20	30	50
21711	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1176	0.0	0.0	0.0	0.0	0.0	0.0	0.0
655	0.0	0.0	0.0	0.0	0.0	0.0	0.0
406	0.1	0.1	0.2	0.2	0.3	0.4	0.5
190	0.7	1.0	1.5	2.2	3.0	3.7	4.8
70	1.6	2.2	3.5	5.0	7.1	8.7	11.2
16	1.8	2.5	4.0	5.7	8.0	9.8	12.7
1	0.6	0.9	1.4	2.0	2.8	3.0	3.0
Sum	4.8	6.7	10.6	15.0	21.3	25.6	32.2

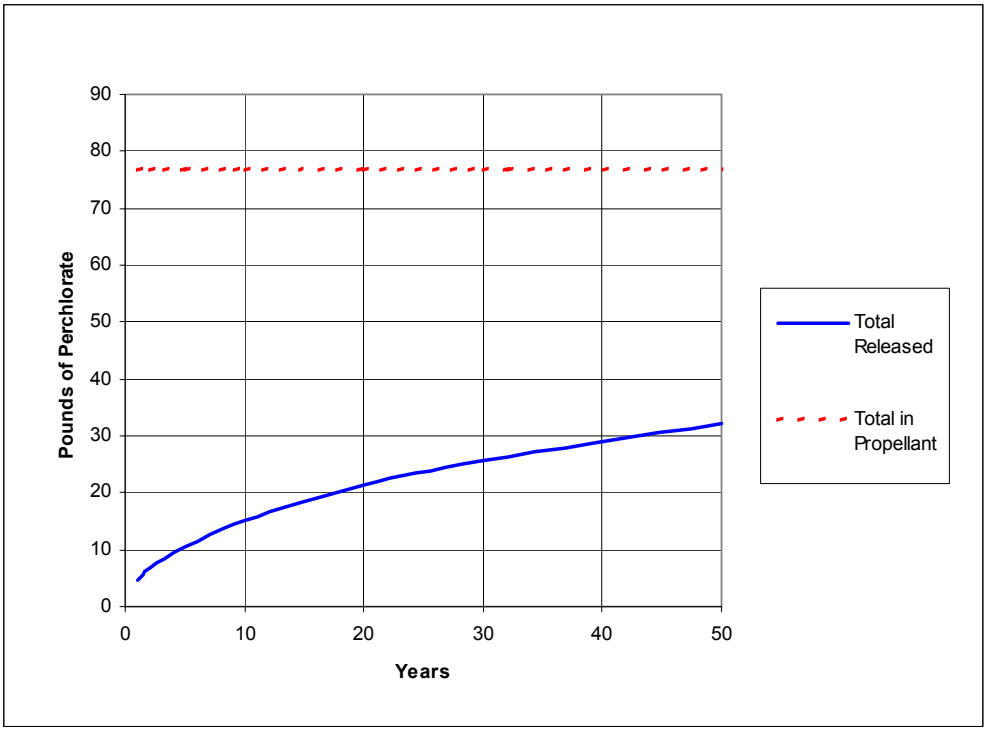

Figure 3.6. Expected cumulative perchlorate release into fresh water lake from 25-s launch destruct; 131 lb propellant entering water.

Table 3.13. Probability Calculation of Perchlorate Released into Fresh Water Lake for Specified Years Following 25-s Launch Destruct; 131 lb Propellant Enter Water

Debris Class	Expected pounds of perchlorate (ClO_4^-) released during a given year						
	1	2	5	10	20	30	50
21711	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1176	0.00	0.00	0.00	0.00	0.00	0.00	0.00
655	0.00	0.00	0.00	0.00	0.00	0.00	0.00
406	0.07	0.03	0.02	0.01	0.01	0.01	0.00
190	0.68	0.28	0.16	0.11	0.08	0.06	0.05
70	1.59	0.66	0.37	0.26	0.18	0.15	0.11
16	1.80	0.74	0.42	0.29	0.20	0.17	0.13
1	0.62	0.26	0.15	0.10	0.07	0.00	0.00
Sum	**4.8**	**2.0**	**1.1**	**0.8**	**0.5**	**0.4**	**0.3**

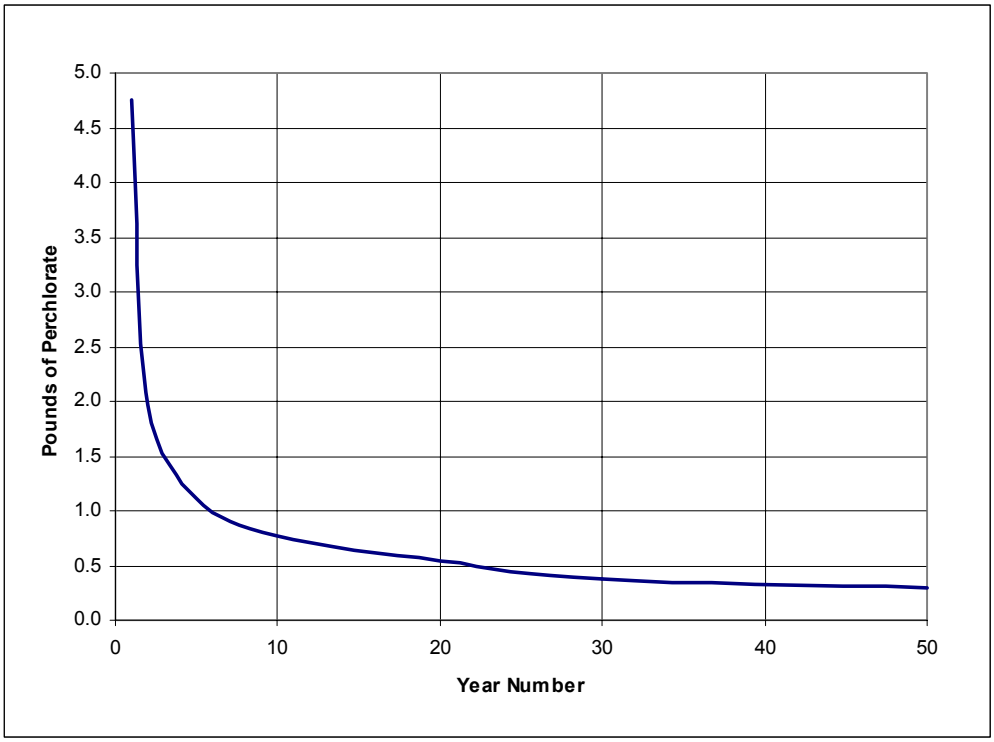

Figure 3.7. Probability perchlorate release into fresh water lake for specific years following 25-s launch destruct; 131 lb propellant entering water.

The debris dispersion modeling predicts that with destruct at 15 s, 100 lb of propellant would be released into the ocean. The probable perchlorate release is calculated for each debris class given in the model. In Table 3.14, the sum is the probable cumulative perchlorate release in pounds during various time periods (in years) commencing from the impact time. This probable cumulative perchlorate release is shown graphically in Figure 3.8. Table 3.15 and Figure 3.9 show the same case expressed with probable mass of perchlorate release calculated for various 12-month periods following the incident.

Table 3.14. Probability Calculation of Cumulative Perchlorate Release into Salt Water (Ocean) from 15-s Launch Destruct, 100 lb Propellant Enter Water

Debris Class	Expected cumulative pounds of perchlorate (ClO_4^-) released during various time spans (years)						
	1	2	5	10	20	30	50
21711	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2183	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1547	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1009	0.0	0.0	0.0	0.0	0.0	0.0	0.0
585	0.0	0.0	0.0	0.0	0.0	0.0	0.0
308	0.3	0.4	0.6	0.9	1.3	1.5	2.0
138	0.8	1.1	1.8	2.5	3.5	4.3	5.6
47	0.9	1.3	2.0	2.8	4.0	4.9	6.4
9.3	0.5	0.8	1.2	1.7	2.4	3.0	3.8
0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sum	**2.5**	**3.6**	**5.6**	**8.0**	**11.3**	**13.8**	**17.8**

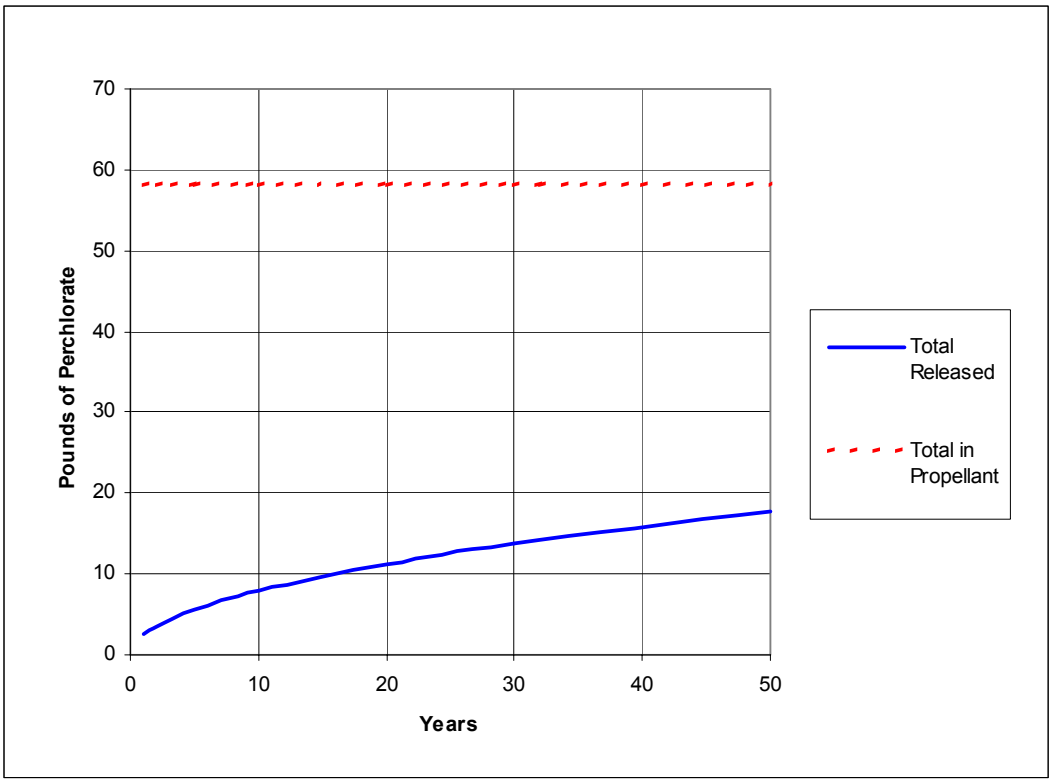

Figure 3.8. Probability calculation of cumulative perchlorate release into salt water (ocean) from 15-s launch destruct; 100 lb propellant entering water.

Table 3.15. Probability Calculation of Perchlorate Released into Salt Water (Ocean) for Specified Years Following 15-s Launch Destruct; 100 lb Propellant Enter Water

Debris Class	Expected pounds of perchlorate (ClO_4^-) released during a given year						
	1	2	5	10	20	30	50
2183	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1547	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1009	0.0	0.0	0.0	0.0	0.0	0.0	0.0
585	0.0	0.0	0.0	0.0	0.0	0.0	0.0
308	0.3	0.1	0.1	0.0	0.0	0.0	0.0
138	0.8	0.3	0.2	0.1	0.1	0.1	0.1
47	0.9	0.4	0.2	0.1	0.1	0.1	0.1
9.3	0.5	0.2	0.1	0.1	0.1	0.0	0.0
0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sum	**2.5**	**1.0**	**0.6**	**0.4**	**0.3**	**0.2**	**0.2**

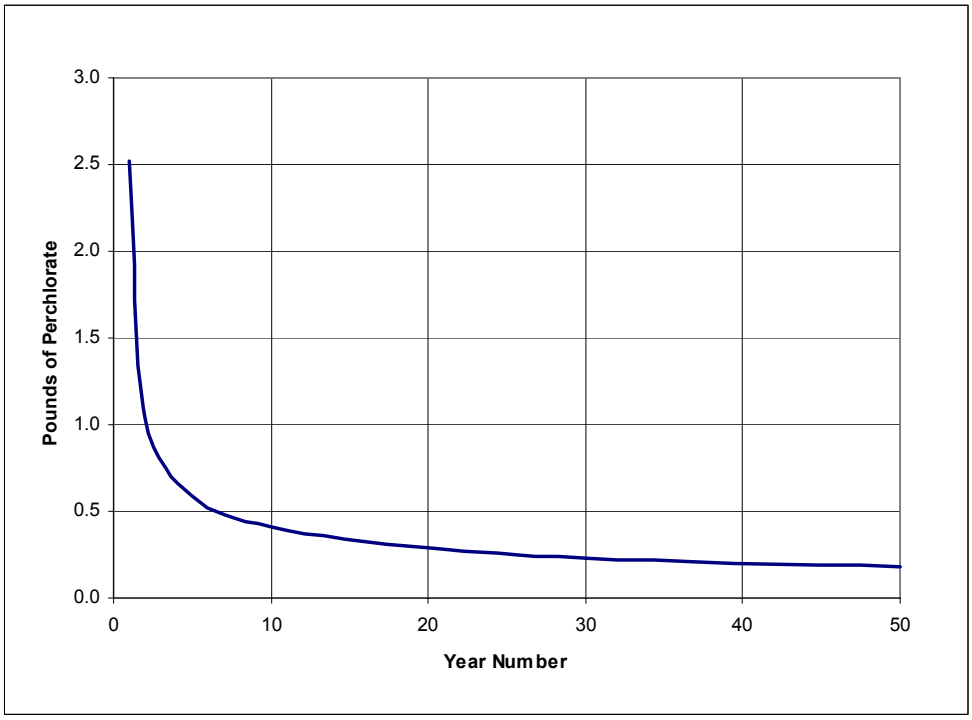

Figure 3.9. Probability calculation of perchlorate released into salt water (ocean) for specified years following 15-s launch destruct; 100 lb propellant entering water.

The debris dispersion modeling predicts that with destruct at 25 s, 41,392 lb of propellant would be released into the ocean. The probable perchlorate release is calculated for each debris class given in the model. In Table 3.16, the sum is the probable cumulative perchlorate release in pounds during various time periods (in years) commencing from the impact time. This probable cumulative

Table 3.16. Probability Calculation of Cumulative Perchlorate Released into Salt Water (Ocean) for Specified Years Following 25-s Launch Destruct; 41392 lb Propellant Enter Water

Debris Class	Expected cumulative pounds of perchlorate (ClO_4^-) released during various time spans (years)						
	1	2	5	10	20	30	50
21711	81.3	114.9	181.7	257.0	363.5	445.2	574.7
1176	22.4	31.7	50.1	70.9	100.2	122.8	158.5
655	30.0	42.4	67.0	94.8	134.1	164.2	212.0
406	53.9	76.3	120.6	170.5	241.2	295.4	381.3
190	86.3	122.0	192.9	272.8	385.8	472.5	610.0
70	103.5	146.4	231.5	327.4	463.1	567.1	732.2
16	85.0	120.3	190.1	268.9	380.3	465.8	601.3
1.0	21.8	30.8	48.8	69.0	97.6	119.5	122.0
Sum	**403.0**	**569.9**	**901.1**	**1274.4**	**1802.2**	**2207.3**	**2817.3**

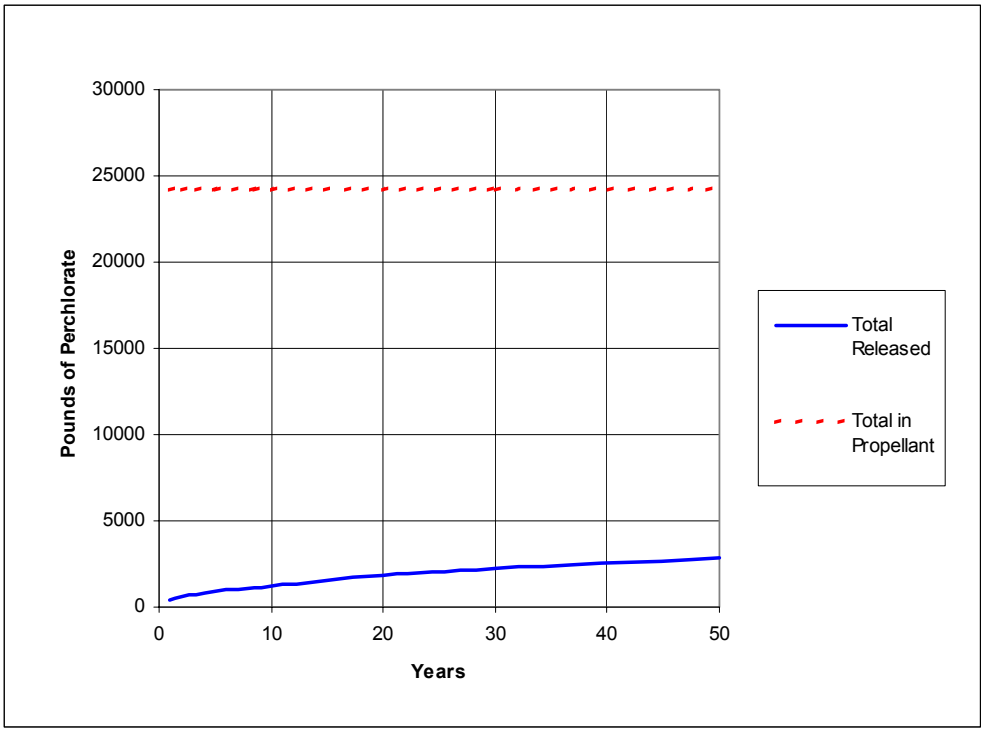

Figure 3.10. Probability calculation of cumulative perchlorate released into salt water (ocean) for specified years following 25-s launch destruct; 41392 lb propellant entering water.

perchlorate release is shown graphically in Figure 3.10. Table 3.17 and Figure 3.11 show the same case expressed with probable mass of perchlorate release calculated for various 12-month periods following the incident.

Table 3.17. Probability Calculation of Perchlorate Released into Salt Water (Ocean) for Specified Years Following 25-s Launch Destruct; 41392 lb Propellant Enter Water

Debris Class	Expected pounds of perchlorate (ClO_4^-) released during a given year						
	1	2	5	10	20	30	50
21711	81.28	33.67	19.19	13.19	9.20	7.48	5.78
1176	22.42	9.28	5.29	3.64	2.54	2.06	1.59
655	29.99	12.42	7.08	4.87	3.40	2.76	2.13
406	53.93	22.34	12.73	8.75	6.11	4.96	3.83
190	86.26	35.73	20.36	14.00	9.77	7.94	6.13
70	103.54	42.89	24.44	16.80	11.73	9.53	7.36
16	85.04	35.22	20.07	13.80	9.63	7.83	6.04
1	21.81	9.04	5.15	3.54	2.47	2.01	0.00
Sum	**403.0**	**166.9**	**95.1**	**65.4**	**45.6**	**37.1**	**27.1**

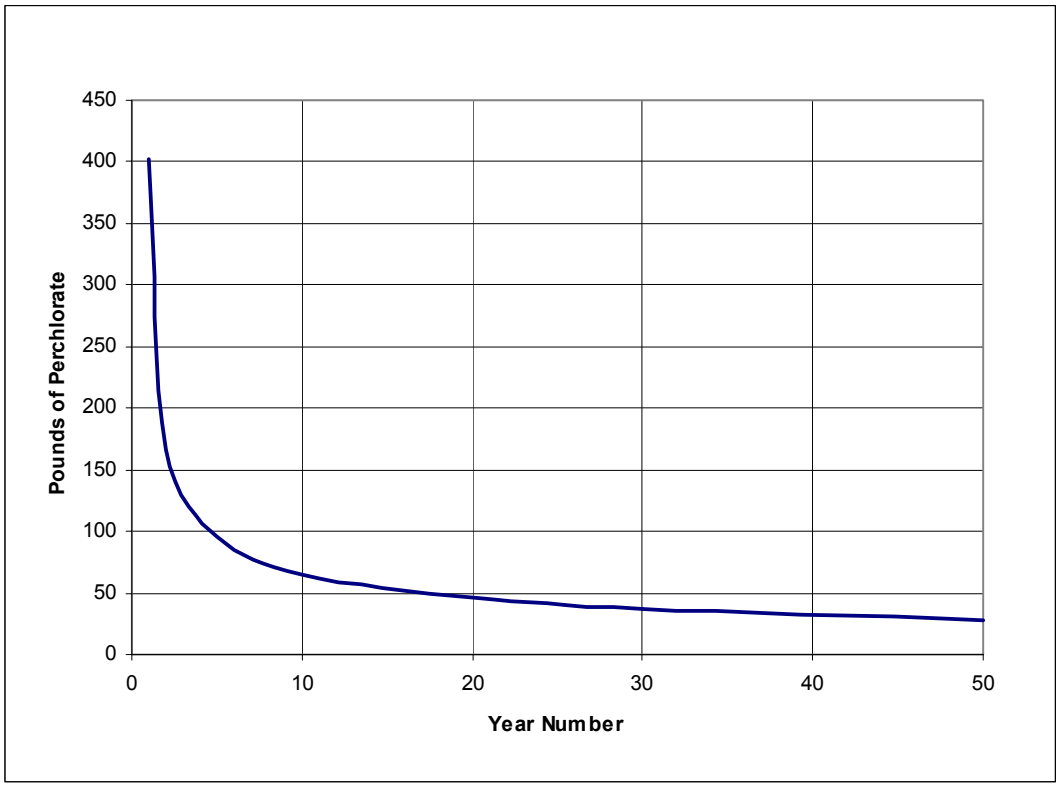

Figure 3.11. Probability calculation of perchlorate released into salt water (ocean) for specified years following 25-s launch destruct; 41392 lb propellant entering water.

Figures 3.12 through 3.15 illustrate how the probable perchlorate release rate is affected by different conditions. These examples use the freshwater lake with 15-s destruct for comparison.

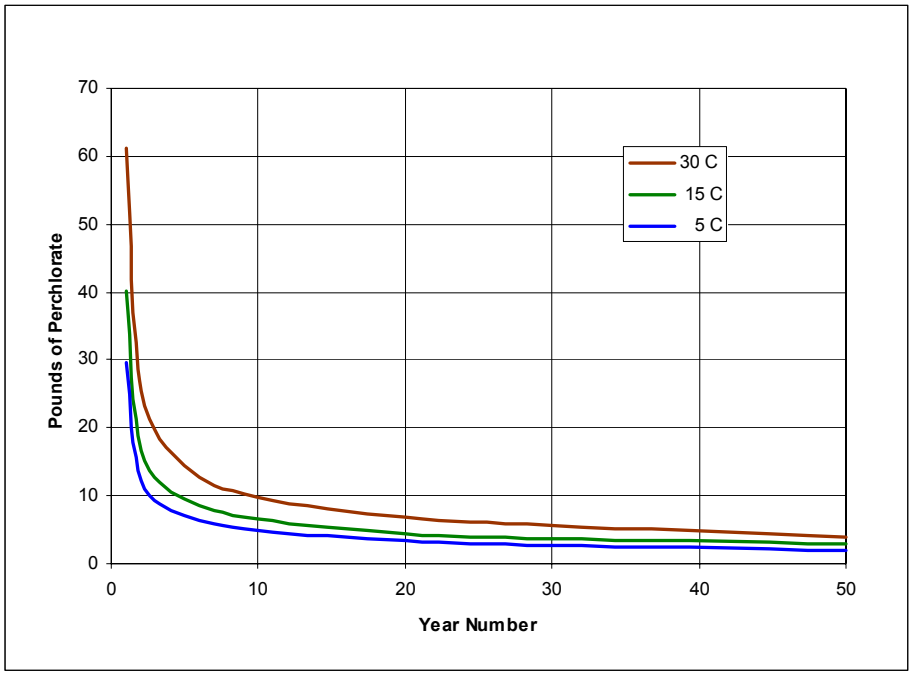

Figure 3.12. Effect of water temperature on probable perchlorate release during a specific year, lake, 15-s destruct, 1805 lb of propellant entering water.

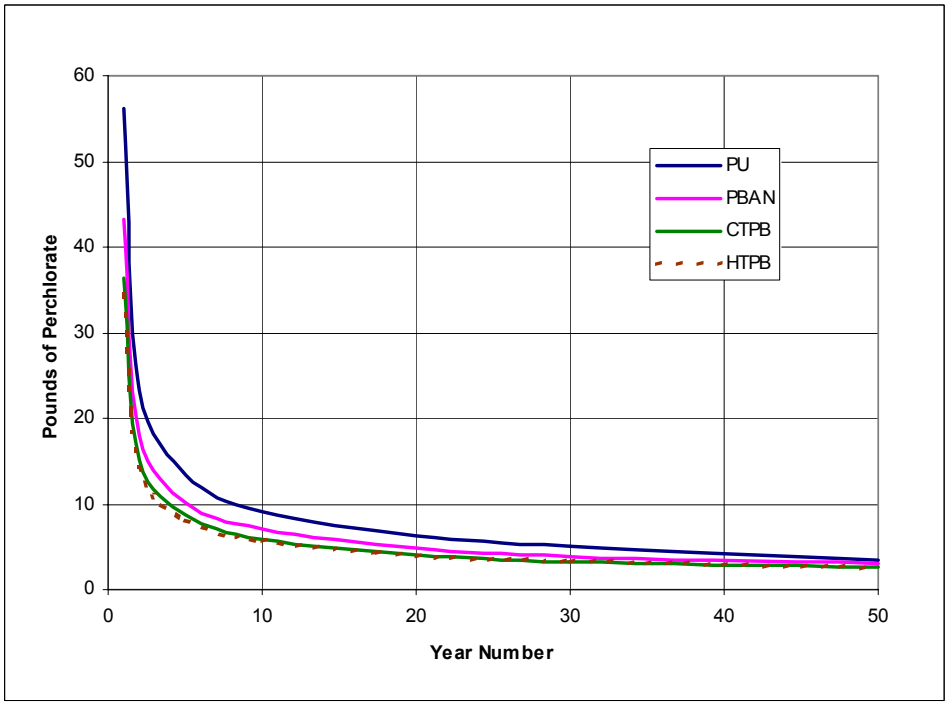

Figure 3.13. Various propellant types in lake. Probable perchlorate release during a specific year for 15-s destruct, 1805 lb of propellant entering water.

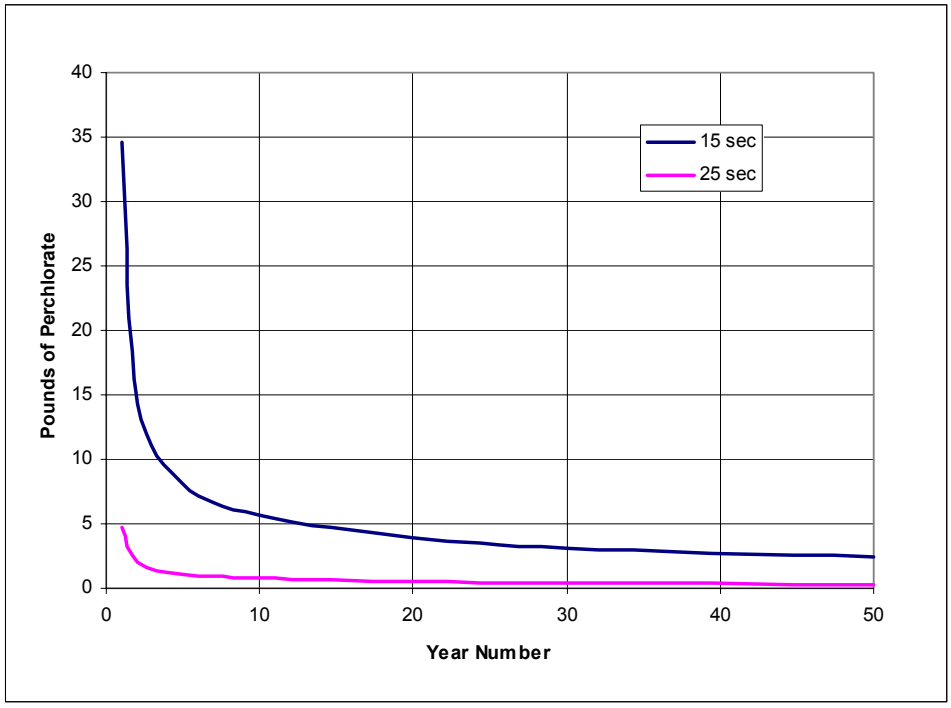

Figure 3.14. Probable perchlorate release into lake. Comparison of 15-s destruct, 1805 lb of propellant entering water, with 25-s destruct, 131 lb of propellant entering water.

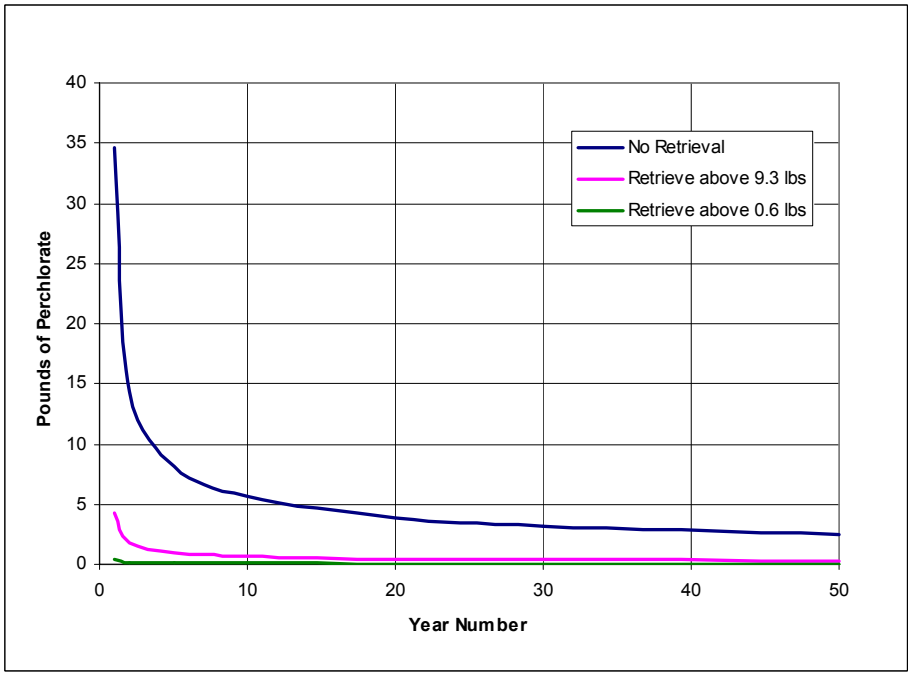

Figure 3.15. Probable perchlorate release into lake. During a specific year, effect of retrieving fragments of larger debris class, 15-s destruct, 1805 lb of propellant entering water.

Increased water temperature causes the release rate to increase. From the chart, it can be seen that in the first year, compared to water at 5°C, at 30°C approximately twice as much perchlorate is expected to be released. This illustrates that a wide seasonal temperature variation of a body of water should be considered in the management decision making process.

Figure 3.13 shows how at the same destruct time and water conditions, the probable perchlorate release rate differs with propellant type.

Figure 3.14 compares 15- and 25-s destruct time results for the lake, showing that a much lower probable perchlorate release rate is expected at 25 s compared to 15 s destruct time. This reflects the fact that at 25 s, more propellant has been consumed by the rocket motor and that the vehicle has moved further down range. Figure 3.15 shows the effect of retrieval of fragments of the larger debris classes on the probable perchlorate release for the lake following a 15-s destruct. The chart shows that removing fragments larger than ~10 lb would significantly reduce the probable perchlorate release.

The perchlorate release rates can be used to estimated the concentration of perchlorate in the water. In a simplistic approach, consider a closed body of well-mixed water that has an inlet flow equal to evaporation and does not have an outlet flow. In this case, the perchlorate concentration would be the cumulative pounds of perchlorate released divided by the pounds of water present. When flow characteristics of the body of water are known, an aqueous dispersion model can be developed to better model the perchlorate concentrations.

3.9 Comparing Perchlorate Concentrations to Environmental Receptors

Each of the U.S. space launch ranges is located in areas containing sensitive environmental species, many of which are listed as threatened or endangered. These have been extensively documented elsewhere, in particular in National Environmental Policy Act studies such as Environmental Assessments and Environmental Impact Studies. Recent biological studies pertaining to perchlorate effects are summarized in a 2002 U.S. Environmental Protection Agency state of the knowledge review.[7]

In the event of an accidental perchlorate release, instantaneous or localized perchlorate concentrations may be higher than long-term steady-state perchlorate concentrations. Or it may take some time for concentrations to build up to a level of concern. In a water system, the concentration will depend on such factors as flow and currents as well as whether the system is closed or open. Precipitation and moisture are important to consider in soil systems.

Toxicity, uptake, and longevity of perchlorate under different environmental conditions and for different species need to be considered in determining effects on receptors. For example, current studies sponsored by the AF at the University of Alaska are investigating the bioaccumulation of perchlorate in soils and the impacts of perchlorate on the development of three-spined stickleback fish.[8]

3.10 Determining Whether Propellant Fragments Should Be Retrieved

Risks associated with the inadvertent release of perchlorate from accidental launch failures must be assessed and managed on a case-by-case basis. The examples in this report illustrate the importance of integrating actual launch vehicle and environmental data with model predictions to make the best decisions possible.

There are numerous variables that should be considered during the planning stages of a launch program to minimize environmental risks from potential perchlorate releases. These include, but are not limited to, propellant type, trajectories, burn time, region of influence (ROI), characteristics of overflight area, biological species present, and temperature of surrounding bodies of water.

It is recommended that a systematic approach to quantifying the potential impacts from an accidental perchlorate release be applied prior to launch. In Sections 2 and 3 we described a step-wise approach to assessing potential impacts from launch failures. Predictive failure probabilities and launch vehicle debris models commonly used for safety analyses are important elements of pre-launch modeling. Certain general considerations can be summarized from the hypothetical case study examples presented in this report.

1. The longer the burn time of the solid rocket motor (and therefore the solid propellant) before failure or destruct, the less perchlorate available for release. This was illustrated by the 25-s destruct vs. the 15-s destruct examples.
2. Marine and fresh water environments need to be considered separately, including variables such as temperature and salinity. For a more detailed analysis, factors such as currents should also be taken into account.
3. Different types of solid propellant (e.g., HTPB, CTPB, PBAN, and PU) release perchlorate at different rates due in large part to different binder characteristics.

For managing and minimizing perchlorate impacts in the aftermath of a catastrophic launch failure, the modeling examples illustrate additional considerations.

1. To quantify perchlorate release, each debris class must be considered separately because the release rates are dependent on the fragment size. Smaller fragments release perchlorate at a faster rate. Actual release rates may be faster than calculated rates due to additional factors such as breakup of fragments by water currents.
2. Large fragments of unburned propellant are easiest to retrieve and can cause the largest cumulative amount of perchlorate to be released over time. See, for example, Tables 3.9 and 3.10.
3. All unburned propellant fragments that land on surfaces where they can be retrieved (for example on accessible pavement or soils) should be retrieved to minimize both short-term and long-term perchlorate release.

4. Annual release rates of perchlorate from fragments of solid rocket propellant generally decline rapidly in early years but persist at lower levels for many years. This is illustrated in Figures 3.5 and 3.6, for example.

5. Release rates of perchlorate from solid propellants immersed in water increase with increasing water temperature.[2]

6. Release rates of perchlorate from solid rocket propellants immersed in water decrease with increasing salinity.[2]

7. Both the total cumulative amount of perchlorate released and the perchlorate released during specified time periods (days, months, years) following a release should be considered in the assessment of potential environmental impacts. Seasonal variations in water temperature and other conditions should be considered.

For pre-launch assessment and planning, a probability distribution of propellant fragments superimposed on a geographic map of the launch site and region of impact down range can be useful. Similarly, probability predictions of perchlorate release in the event of a failure can be used to assess risks from the program. For the examples given in Subection 3.8.1 (where the probability of a failure was assumed to be one) release rates for each debris class were calculated separately and summed to give the total probability of release expected over various time periods commencing from the impact. Figures 3.4 –3.11 also illustrate the trends of short-term perchlorate releases vs. long-term releases.

For post-failure assessment and mitigation, more specific information about propellant fragment sizes, the number of fragments, and their distributions may be known from actual observations. Estimating an upper limit to the total mass of released propellant and perchlorate may be desirable. The modeling approach can be tailored to address perchlorate release from specific size fragments under specific environmental conditions.

4. Managing Risk Associated with Potential Release of Perchlorate from Launch Operations

As illustrated by our hypothetical case study, risks associated with the inadvertent release of perchlorate from accidental launch failures must be managed on a case by case basis because of the complexity of variables that can affect the release rate from propellants, and because each launch location has unique environmental characteristics. The same type of approach can be used to assess the risk of perchlorate releases from other operations where sold propellant may be dispersed.

We recommend that a systematic approach to assessing potential impacts be used in the initial planning stages of a launch program, for example, in the AF Environmental Impact Analysis Process, which complies with the National Environmental Policy Act (NEPA). Regulatory agencies may require such analyses be performed prior to new launch programs. In this report, we have presented one type of step-wise approach to assessing perchlorate releases for a typical launch scenario.

Initial studies performed by the University of Alaska on fish exposed to solid propellant in water samples, and in particular on fish exposed to perchlorate in water, indicate the potential for significant biological effects.[8] Studies are also under way to determine the effect of released perchlorate on soil and plant species.[9]

Some general considerations in the management of accidental perchlorate releases can be implied from the results of our earlier chemical kinetics laboratory studies, our debris modeling, and the hypothetical case study of perchlorate release from a launch failure. These considerations are illustrated in Section 3.

1. In determining perchlorate release, each debris class must be considered separately because the release rates are dependent on fragment size. Smaller fragments release perchlorate at a faster rate. Actual release rates may be faster than those calculated rates due to factors not readily quantifiable, such as breakup of fragments by water currents.

2. Large fragments of unburned propellant are easiest to retrieve and can cause the largest cumulative amount of perchlorate to be released.

3. All fragments that land on surfaces where they can be retrieved (e.g., on accessible soil or pavement) should be retrieved.

4. The longer the burn time of the solid rocket motor (and therefore the propellant contained within) before failure or destruct, the less perchlorate available for release. (See 25-s destruct vs. 15-s destruct.)

5. Annual release rates of perchlorate from fragments of solid rocket propellant generally decline rapidly in early years but persist at lower levels for many years (see Tables 3.13 and 3.15 and Figures 3.7 and 3.9, for example).

6. Release rates of perchlorate from solid rocket propellants immersed in water increase with increasing water temperature.[1]

7. Release rates of perchlorate from solid rocket propellants immersed in water decrease with increasing salinity.[1]

8. Both the total cumulative amount of perchlorate released and the perchlorate released during specified time periods (e.g., days, months, years) following a release should be considered in the assessment of potential environmental impacts.

5. Summary

The example scenarios illustrated in this report serve to demonstrate how impact debris distributions, debris models, and actual chemical kinetics data can be combined to quantify and determine likely locations of potential perchlorate releases in the event of a launch failure. Both pre-launch planning and post-failure analyses can be performed by using empirical data in the models we have developed. The step-wise approach to assessing such releases should be tailored to specific launch parameters and locations. Specific concerns relevant to managing risks to the environment, such as comparing short-term vs. long-term release scenarios, can also be addressed. When combined with data on biological species of interest and geophysical parameters, the method presented here can be an effective tool in the management of potential perchlorate releases from launch operations.

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Appendix—Analysis of Laboratory Water Samples: Water-Extractable Materials from Solid Propellants

A1. Introduction

In earlier phases of this study, laboratory experiments were conducted to determine the rates at which perchlorate is released from solid rocket propellants immersed in water, and the influence of temperature and salinity on the rates.[1,2] In the most recent laboratory studies, different solid propellants were studied in various water samples at different temperatures. The water samples in which the propellants were immersed have since been analyzed for substances other than perchlorate, which may have leached out of the samples during the experiments.

The solid propellants contain, in addition to ammonium perchlorate, a number of other substances. This study was conducted to determine which of the other ingredients or hydrolysis products are leached out into the water for future assessment as to their potential environmental impact. This laboratory study consisted of identifying the materials extracted by the water at 30°C in which four different solid propellants were immersed for 11 months by analyzing the water or dry residue with infrared spectroscopy (IR), solid-probe mass spectrometry (SP-MS), and inductively coupled plasma mass spectrometry (ICP-MS).

A2. Solid Propellants

The propellants used in this study are composite-base propellants containing ammonium perchlorate (AP) oxidizer, and aluminum (Al) fuel held in a synthetic rubber matrix or binder that holds the propellant together. Table A-1 lists the ingredients of the four propellants used in this study. The ingredients listed are before the propellant was cured, and many of these materials would not be present as such in the propellant. The binder and curative will be consumed by the reaction to produce the rubber matrix. Only traces, if any, of unreacted material might be present. The materials expected to be present in the water are those ingredients that are un-reacted and hydrolysis products.

The solid propellants are often classified by the type of rubber binder used, and many solid rocket motor systems use the same type of propellants. The propellant/water samples used in this study were those used in the earlier chemical kinetics experiments:[2]

(a) Hydroxyl-terminated polybutadiene. The binder based on the hydroxyl terminated polybutadiene (HTPB) is the most common modern propellant type. For this study, it was designated HD-30. The cure reaction involved the R-45M and both isocyanates, dimeryl diisocyanate (DDI), and the isophorone diisocyanate (IPDI) to produce a polyurethane rubber matrix.

(b) Carboxy-terminated polybutadiene. Carboxy-terminated polybutadiene (CTPB) was the binder that was used before HTPB became more common. For this study, it was designated CD-30. The cure reaction involved the CTPB with the HX-868 – butylene imine derivative of trimesic acid (BITA).

(c) Polybutadiene Acrylic Acid Acrylonitrite. Polybutadiene acrylic acid acrylonitrile (PBAN) binder is also used in some propellants. For this study, the propellant was designated PD-30. The cure reaction is between the PBAN and the epoxy resin.

(d) Polyurethane. The polyurethane (PU) type propellant was designated UD-30 for this study. The cure reaction is between the polypropylene glycol (PPG) and the toluene-2,4-diisocyanate (TDI).

The other ingredients in the propellants are added to impart specific properties or to prevent oxidation. In the HTPB propellant, the triphenyl bismuth (TPB) was added to catalyze the cure reaction. The dioctyl sebacate (DOS) and other plasticizers impart better mechanical properties. The tetraethylene tetraamine (TET) and the DER332 epoxy resin are added to better bind the AP with the rubber matrix. They are referred to as wetting agents. The iron oxide was added as a burn rate enhancer.

Table A1 lists the components of the solid propellants analyzed by weight percentage, as provided by Space and Missile Propulsion Branch, Missile Technology Division, Air Force Research Laboratory, where the propellant samples were prepared. This characterization of the propellants was used in our earlier chemical kinetics analyses.[2]

Table A1. Ingredients of solid propellants used in this study.

HD-30 (HTPB)	**Purpose**	**Weight %**
AP 20 μ, ammonium perchlorate	oxidizer	19.00 %
AP 200 μ, ammonium perchlorate	oxidizer	50.00 %
Al 29μ, aluminum	fuel	19.00 %
R-45 M, hydroxyl terminated polybutadiene (HTPB)	binder	9.03 %
DDI, dimeryl diisocyanate	curative	0.25 %
IPDI, isophorone diisocyanate	curative	0.52 %
DOS, dioctyl sebacate	plasticizer	2.00 %
DER332, epoxy resin	AP wetting	0.06 %
TET, Tetraethylene tetraamine	AP wetting	0.04 %
TPB, triphenyl bismuth	catalyst	0.01 %
AO 2246, 2,2'-methylene-bis-(4-methyl-6-tert-butyl) phenol	anti-oxidant	0.09 %
CD-30 (CTPB)		
AP 200 μ, ammonium perchlorate	oxidizer	51.10 %
AP 17-20 μ, ammonium perchlorate	oxidizer	21.90 %
Al 17-20 μ, aluminum	fuel	15.00 %
Butarez-CTL, carboxy terminated polybutadiene (CTPB)	binder	8.56 %
HX-868, butylene imine derivative of trimesic acid (BITA)	curative	0.44 %
Oronite 6, polybutene molecular weight ~300	plasticizer	3.00 %
AO 2246, 2,2'-methylene-bis-(4-methyl-6-tert-butyl) phenol	anti-oxidant	
PD-30 (PBAN)		
AP 20 μ, ammonium perchlorate	oxidizer	20.93 %
AP 200 μ, ammonium perchlorate	oxidizer	48.85 %
Al 13μ, aluminum	fuel	16.00 %
PBAN, Polybutadiene acrylic acid acrylonitrile	binder	12.15 %
Epoxy resin	curative	1.85 %
Fe_2O_3, Iron oxide	burn rate modifier	0.22 %
UD-30 (PU)		
AP 20 μ, ammonium perchlorate	oxidizer	17.21 %
AP 200 μ, ammonium perchlorate	oxidizer	48.16 %
Al 13μ, aluminum	fuel	17.00 %
PPG, polypropylene glycol	binder	8.65 %
TEA, trimesol-1-(2-ethyl) aziridine	curative	0.21 %
TDI, toluene-2,4-diisocyanate	curative	2.05 %
IDP, isodecyl pelargonate	plasticizer	0.27 %
TMG*		4.36 %
Carbon Black	filler	0.20 %
AO 2246, 2,2'-methylene-bis-(4-methyl-6-tert-butyl) phenol	anti-oxidant	0.12 %
FeAA, ferric acetylacetonate		0.04 %
DC-200, silicone oil		0.01 %
DOZ, dioctyl azelate	plasticizer	1.73 %

*No additional information available

A3. Experimental

The propellant specimens were cylindrical in shape, with a height and diameter of approximately 14 mm for both dimensions, and the weight of each was approximately 4 g. These samples were immersed in 500 ml of water at 30°C and were used in earlier chemical kinetics experiments.[2] The samples were originally placed in the water on 5/29/02 and left undisturbed in the oven at the control temperature after the perchlorate rate study was completed. A 100 ml aliquot of each aqueous solution was removed on 4/22/03 for this study; therefore, the total propellant exposure time was 11 months.

The aqueous solutions were either analyzed as is, or the water was removed to dryness using a desiccant so that the sample was not heated. This method prevented evaporation of volatile components. The dried residue was extracted with toluene to dissolve the organic materials and not the AP.

A3.1 Inductively Couple Plasma Mass Spectrometry (ICP-MS)

The quantitative analyses by ICP-MS of the elements aluminum (Al), iron (Fe), bismuth (Bi), and silicon (Si) were performed by West Coast Analytical Services, Inc. The aqueous solutions with no further treatment were sent for analysis.

The toluene extracts of the dried aqueous residues were examined by FTIR using the attenuated total reflectance technique (ATR). The IR spectrometer is a Nicolet Magna 550 equipped with a DTGS detector and Nicolet's OMNIC™ FTIR software. The ATR was obtained with a DuraScope attachment that has a one-bounce diamond Duradisk. Spectra were recorded at a resolution of 4 cm^{-1} from 4000 to 650 cm^{-1} and co-adding 150 scans. A literature search of the obtained spectra was performed to identify the extracted materials.

A3.2 Solid-Probe Mass Spectrometry (SP-MS)

The toluene extracts of the dried aqueous residues were examined by SP-MS. The mass spectrometer was a Kratos MS-25RF magnetic sector interfaced with a Sparc 5 Sun Station and Kratos Mach 3 data system for instrument control and data processing. The toluene sample was placed into a capillary tube and the toluene allowed to evaporate. This capillary tube was placed into the SP that can be temperature programmed and was set to heat from room temperature to 300°C at a rate of 10°C/min. The SP was inserted into a vacuum lock with a ball valve that allows the sample into the source of the spectrometer that is at a pressure of 10^{-6} Torr. The spectrometer collects full mass spectral scans (15–600 amu) at a rate of approximately 6 scans per minute. Literature searches of the following databases were performed to interpret the spectra:

- Eight Peak Index of Mass Spectra, 1991 fourth edition.
- EPA/NIH Mass Spectra Data Base, 1978

- Integrated Spectral Data Base (SDBS), from the National Institute of Advanced Industrial Sciences and Technology, Tsukuba, Ibaraki, Japan.
- NIST Chemistry book on line databases.

A4. Results and Discussion

The aqueous solutions were analyzed by ICP-MS for aluminum (Al), bismuth (Bi), iron (Fe), and silicon (Si). This technique detects elements by mass spectrometry. The analysis was performed by West Coast Analytical Services, Inc. Attachment A1 is the laboratory report. The sample ID as BD-30 in the laboratory report was only distilled water (i.e., a blank sample) of the type used to immerse the propellant samples. The propellant formulations indicate that all four propellants contain Al; PD-30 and UD-30 contain Fe; HD-30 contains Bi as TPB, and UD-30 contains Si in the DC-200 silicon oil. The summarized results of the ICP-MS analysis are given in Table A2. The concentration of Al detected in the aqueous solutions was significantly lower than expected from the % in the propellant. This indicates that the Al was trapped in the rubber matrix of the solid propellants. The PU binder seems to be the least efficient in trapping the Al. No Fe was detected from the PBAN propellant while the Fe from the ferric acetyl acetonate was detected from the PU propellant. Bi was detected from the HTPB propellant, indicating that the TPB does dissolve in the water; however, the concentration was significantly lower than the % TPB in the propellant would indicate. The Bi detected in the CD-30 sample is less than in the BD-30 or blank; therefore, the Bi is not from the propellant. Attachment A2 shows a calculation of the expected concentrations for the Al, Fe, and Bi if they were leached at the same rate as the AP. The AP concentrations were determined for 60 days exposure; therefore, for the 11 months exposure, a higher concentration of the elements and AP would be expected. In conclusion, the other materials are leached out at a significantly lower rate, almost 1000 times lower than predicted from the concentration of the AP.

Table A2. ICP-MS Results of the Aqueous Solutions of the Solid Propellants

Propellant	Aluminum (mg/l)	Bismuth (mg/l)	Iron (mg/l)	Silicon (mg/l)
HD-30	1.23	0.0006	ND	ND
CD-30	0.083	ND	ND	ND
PD-30	0.034	ND	ND	ND
UD-30	2.1	ND	0.11	ND

An aliquot of 25 ml of the aqueous solutions of the four solid propellants listed in Table A1 were evaporated to dryness, and the residue weighed. The concentration of the extractable was calculated from the dry weight. Results are given in Table A3. The main extracted material from the following solid propellant is the AP. The residue concentrations follow the AP % in the propellant.

Table A3. Concentration Of All Solids In The Aqueous Solutions

Propellant	% AP in propellant from formulation	Residue concentration (mg/l)
HD-30	69.00	6630
CD-30	73.00	7480
PD-30	69.78	7120
UD-30	65.37	6240

The other residues that could be extracted by the water would be organic materials. These materials are expected to be soluble in organic solvents like methylene chloride and toluene while the AP is not. The methylene chloride, however, did not extract enough material to be weighed. The same dry residue was extracted with toluene. The residues from the toluene extract were weighed, and the concentrations obtained are given in Table A4. The residue from CD-30 and PD-30 is very small and might not be sufficient to obtain good results. The toluene-extractable materials were analyzed by FTIR and solid-probe mass spectrometry (SP-MS). The materials detected are also listed in Table 4.

Table A4. Organic Residue Extracted by Toluene from the Dried Aqueous Extract of the Solid Propellants

Propellant	Residue concentration (mg/L)	Materials detected by SP-MS	Materials detected by FTIR
HD-30	0.015	Triphenylbismuth	Triphenylbismuth
CD-30	0.004	phthalate	Siloxane
PD-30	0.004	Methyl methacrylate	Epoxy resin
UD-30	0.016	DOZ FeAA	Propylene glycol DOZ IDP 4-hydroxy-2-pentanal

A4.1 HD-30 (HTPB Propellant)

Figure A1 shows the FTIR of the residue from the toluene-extracted aqueous dried residue of the HTPB propellant. The literature search results for the top 10 matches for possible materials are given in Figure A1a. None of the materials listed in the library search are among the propellant ingredients listed in Table A1 nor are they expected hydrolysis products. The ICP-MS detected bismuth in the aqueous solution; therefore, some TPB or its hydrolysis products can be expected in the residue. The IR spectrum of TPB is shown in Figure A2, and the two intense absorption peaks at 690 and 720 cm^{-1} are also found in the residue from the HTPB propellant. This indicates that some TPB was leached out from the propellant. DOS and AO 2246 are also materials that could leach out into the water from the HTPB propellant since they do not react with other propellant ingredients. The FTIR spectra of DOS and AO 2246 are shown in Figure A2; however, none of their main absorptions are found in the residue from the propellant.

The total ion chromatogram (TIC) of the SP-MS analysis of the residue from the toluene-extracted aqueous dried residue from the HTPB propellant is shown in Figure A3. The mass spectra at scans 70, 90, and 100 are also shown in Figure A3. The spectra at scans 90 and 100 show masses at 277, 199, 201, 152, 77, etc. The mass spectra of the TPB, DOS, and AO 2246, which are possible extractable materials, are shown in Figure A4. None of these three compounds was found as possible materials in the residue by SP-MS because the main peaks were not found in the spectra of the toluene-extracted residue of the aqueous residue from the HTPB propellant shown in Figure A3. The SDBS library search indicated that triphenylphosphine oxide (TPO) has a mass spectrum with some of those masses. This material is not listed as an ingredient and is not a possible hydrolysis product from TPB; however, it also appeared in the FTIR search results. This could be a coincidence or it might be that TPO is an impurity in a propellant ingredient. The additional low mass 43, 55, 69, 83, 97, 149, etc. at scan 70 indicates that other materials are also present; however, they have not been identified. The other propellant ingredients are even less likely to be leached out, and only hydrolysis products are possible. The DDI and the IPDI react with the R45M to form the rubber matrix, and only traces, if any, might be present in the propellant. No mass peaks were found to indicate the presence of IPDI—the only available mass spectrum. Also, the isocyanate group is reactive with water, and the hydrolysis product would be the material present. TET reacts with the DER 332 epoxy resin, and only traces, if any, are expected in the propellant. No masses that would have identified the TET in the residue were found.

A4.2 CD-30 (CTPB Propellant)

Figure A5 shows the FTIR of the residue from the toluene-extracted aqueous dried residue from the CTPB propellant. The library search results indicated the presence of polydimethylsiloxane with a match index of 88.13; however, the formulation does not list a silicon-containing material as an ingredient, and the ICP-MS also indicates that there is no Si in the aqueous solution. This is, therefore, not a realistic result. The residue from this sample is very small, and sample contamination could be possible.

The TIC of the SP-MS analysis of the residue from the toluene-extracted aqueous dried residue from the CTPB propellant is shown in Figure A6. The mass spectra at scans 65, 90, and 145 are also shown in Figure A6. The spectrum at scan 90 shows masses at 149 and 167. These masses are typical of phthalate compounds that are used as plasticizers; however, no phthalate was listed as a propellant ingredient. No other materials have been identified from the spectra. The HX-868 reacts with the Butarez-CTL to form the rubber matrix, and only traces, if any, are expected in the propellant. The AO 2246 was not detected—the mass spectrum shown in Figure A4. No standard or mass spectrum was found for Oronite 6 to determine whether it was leached out from the propellant.

A4.3 PD-30 (PBAN Propellant)

Figure A7 shows the FTIR of the residue from the toluene-extracted aqueous dried residue from the PBAN propellant. The library search results indicated the presence of DER 667 with a match index of 85.37. The designation DER corresponds to an epoxy resin from Dow Chemical Co., and this propellant contains an epoxy resin as an ingredient.

The TIC of the SP-MS analysis of the residue from the toluene-extracted aqueous dried residue from the PBAN propellant is shown in Figure A8. The mass spectra at scans 60, 80, 150, and 200 are also shown in Figure A8. A search of the SDBS database for masses 100, 69, and 41 show that methyl methacrylate is a possible material in the residue. The methyl methacrylate could be a hydrolysis product of the PBAN-Epoxy binder matrix or a thermal decomposition product as the result of the analysis since the probe temperature was about 150°C at the scans where the masses were observed. The library search for masses 199, 91, and 92 did not give reasonable material among the possible compounds.

A4.4 UD-30 (PU Propellant)

Figure A9 shows the FTIR of the residue from the toluene-extracted aqueous dried residue from the PU propellant. The library search results indicated the presence of propylene glycol ricinoleate with a match index of 75.31. This is a possible material since the binder for this propellant is PPG. The FTIR spectrum of FeAA is shown in Figure A10. Comparison with the obtained spectrum of the residue indicates that the intense peaks in FeAA in the 1500 cm^{-1} region are not present. Therefore, the FTIR did not show the presence of FeAA. The FeAA could hydrolyze and form an alcohol (4-hydroxy-2-pentanal). The FTIR spectrum of 3-acetyl-1-propanol is shown in Figure A10, which will be similar to 4-hydroxy-2-pentanal. The 4-hydroxy-2-pentanal does have a strong carbonyl absorption in the 1700 cm^{-1} region and does match the carbonyl absorption in the residue from the propellant. Also notice that the residue has absorption in the alcohol (OH) 3500 cm^{-1} region. It is likely that the 4-hydroxy-2-pentanal is the leached out material from FeAA. The FTIR spectra of DOZ and IDP were not found. Both materials are esters, and their spectra should be similar to that of ethyl pelargonate shown in Figure A10. Note that the pelargonate carbonyl band at approximate 1700 cm^{-1} region is at a higher wavelength than the carbonyl from the 4-hydroxy-2-pentanal. Also notice that the carbonyl of the propellant residue is wider in intensity than the individual pelargonte or 4-hydroxy-2-pentanal; therefore, it is possible that the propellant residue contains both materials. The TIC of the SP-MS analysis of the residue from the toluene-extracted aqueous dried residue from the PBAN propellant is shown in Figure A11. The mass spectra at scans 60, 90, and 110, are also shown in Figure 11. No mass spectrum is available for PPG, IDP, and 4-hydroxy-2-pentanal to determine their presence in the residue. The mass spectra of DOZ and FeAA are shown in Figure A11a. The mass at 171, main mass of DOZ, and mass 254, main mass in FeAA, can be observed in scan 110 at very low intensity. This indicates their presence; however, they are not the main extracted materials.

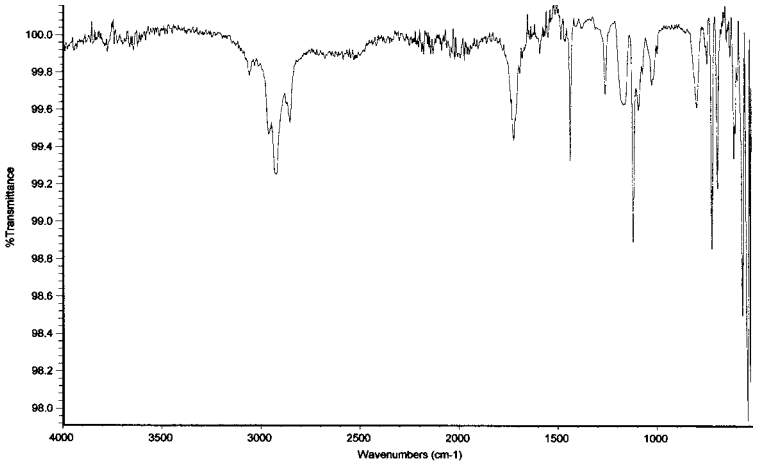


Figure A1. FTIR spectrum of the residue from the toluene extracted aqueous dried residue of the HTPB propellant.

	Index	Match	Compound Name	Library Name
1	1133	73.89	COMPLEX of Rh(I); TRIS(TRIPHENYLPHOSPHINE)RHODIUM CHLORIDE	HR Inorganics
2	3950	71.77	Chlorohydridotris(triphenylphosphine)ruthenium(	HR Aldrich Condensed Phase
3	8865	71.17	Triphenylphosphine oxide	HR Aldrich Condensed Phase
4	9128	59.75	Bis(triphenylphosphoranylidene)ammonium borohydride, 97%	HR Aldrich Condensed Phase
5	3864	50.05	Nitrosyltris(triphenylphosphine)rhodium(I)	HR Aldrich Condensed Phase
6	2805	49.26	Tris(triphenylphosphine)rhodium(I) bromide	HR Aldrich Condensed Phase
7	4558	45.03	Triphenyltin hydroxide	HR Aldrich Condensed Phase
8	534	44.79	PHTHALO BL50-991-037	Industrial Coatings
9	4045	44.77	(2-(1,3-Dioxolan-2-yl)ethyl)triphenylphosphonium romide	HR Aldrich Condensed Phase
10	8813	43.83	Bromomethyltriphenylphosphonium bromide, 98%	HR Aldrich Condensed Phase

Figure A1a. List of literature search results.

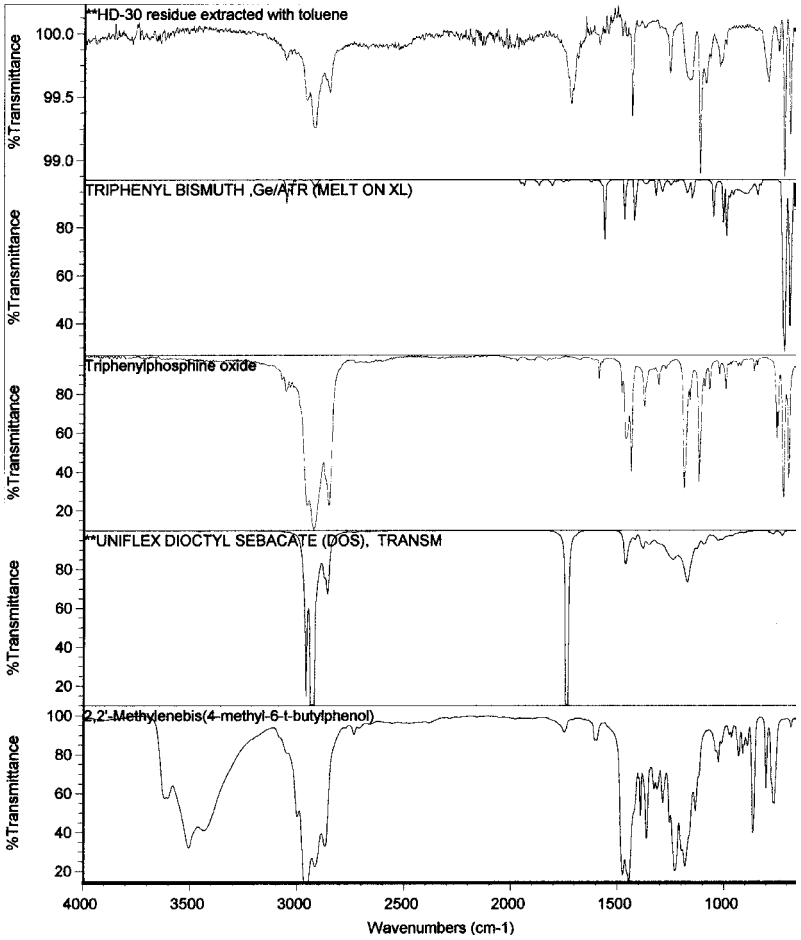
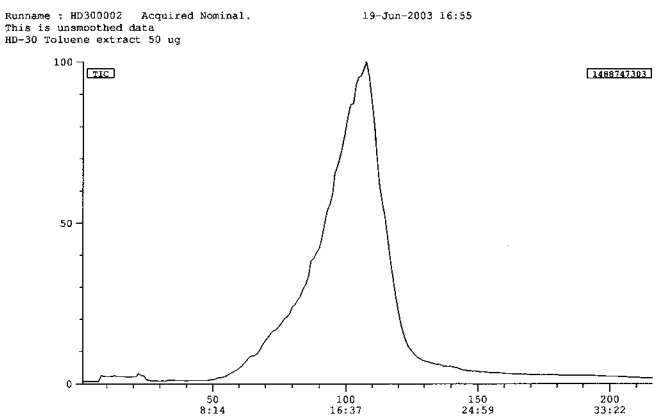
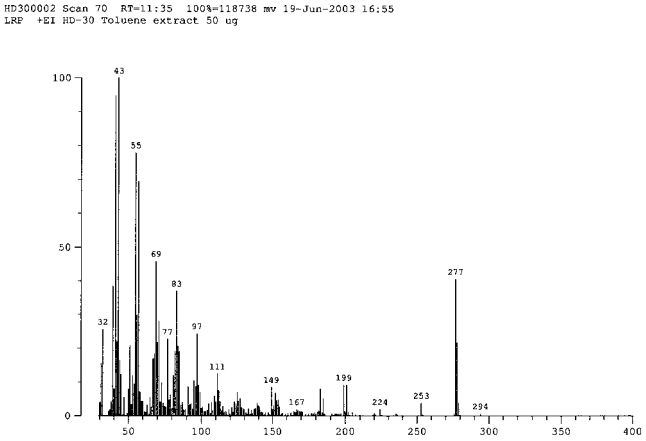


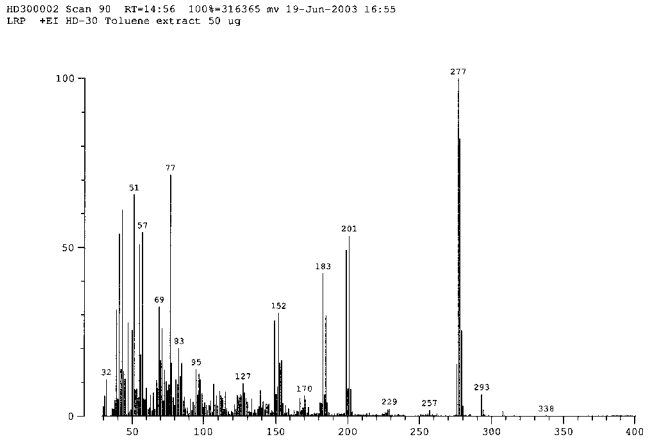
Figure A2. FTIR spectra of TPB, TPO, DOS, AO 2246, and the toluene extract from the dried residue of the aqueous extract from HTPB propellant.



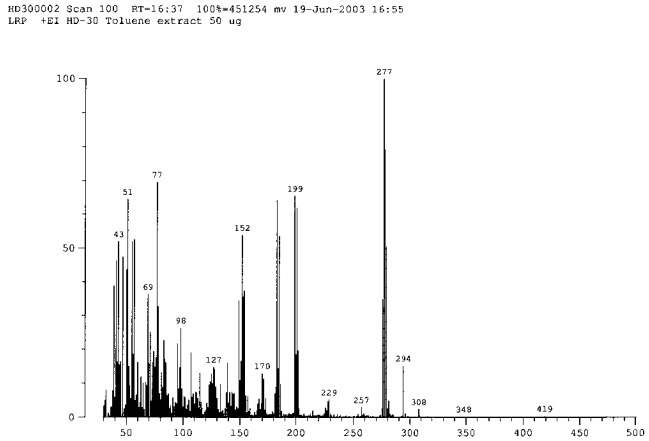
TIC



Scan 70



Scan 90



Scan 100

Figure A3. TIC of the SP-MS Analysis of the Toluene Extracted Residue of the Aqueous Residue from the HTPB Propellant and Mass Spectra at Scans 70, 90, and 100.

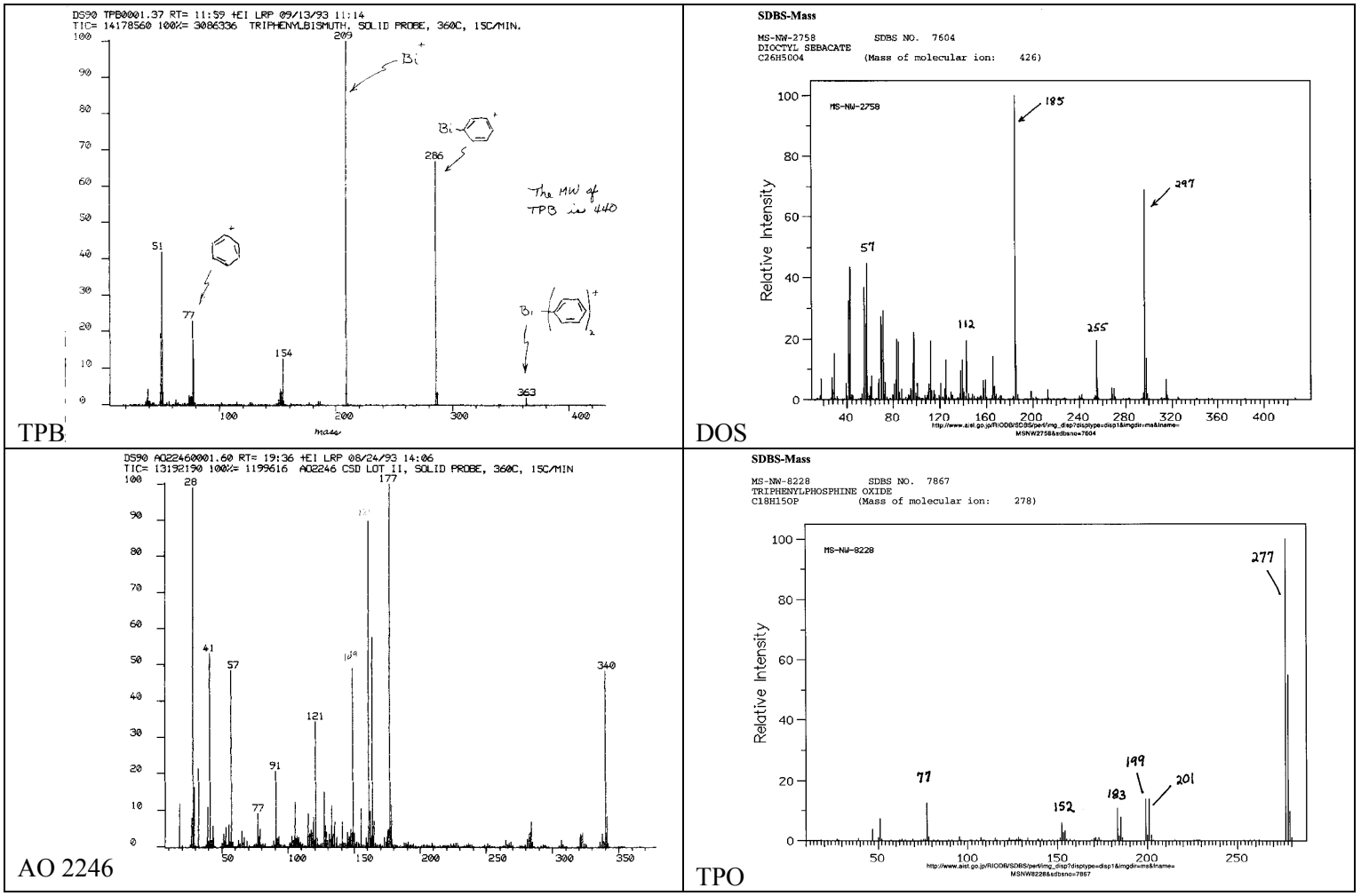


Figure A4. Mass spectra of standards TPB, DOS, AO 2246 and TPO.

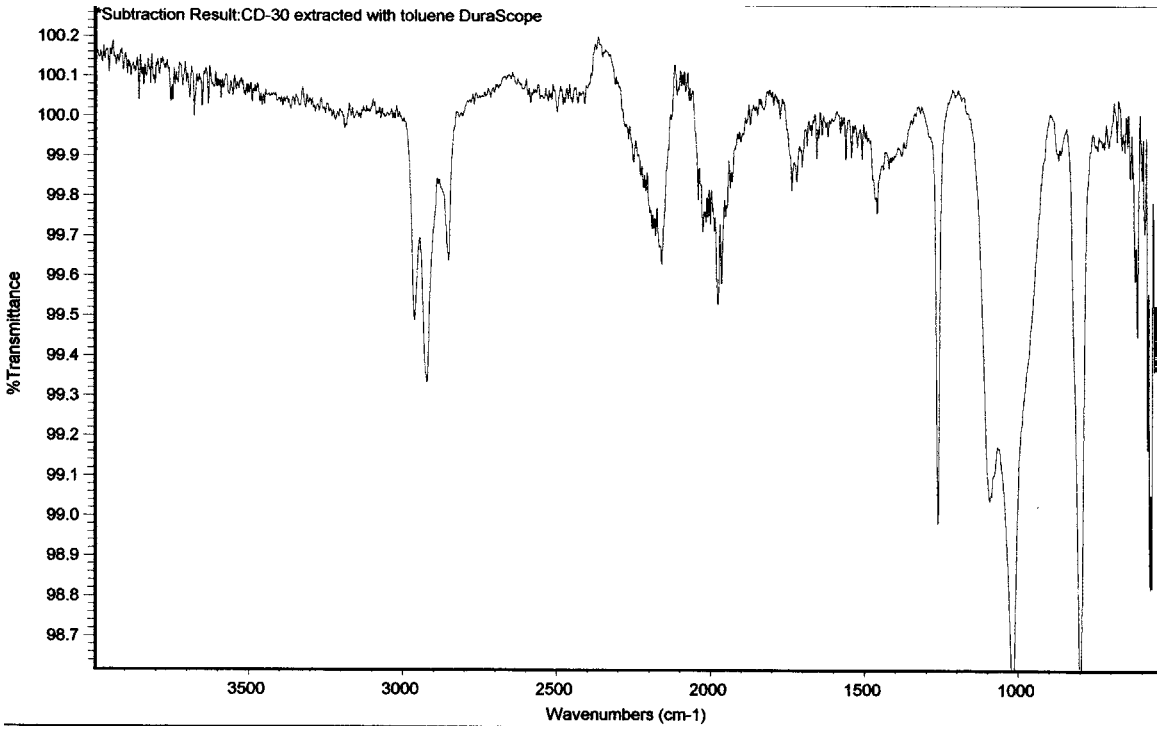
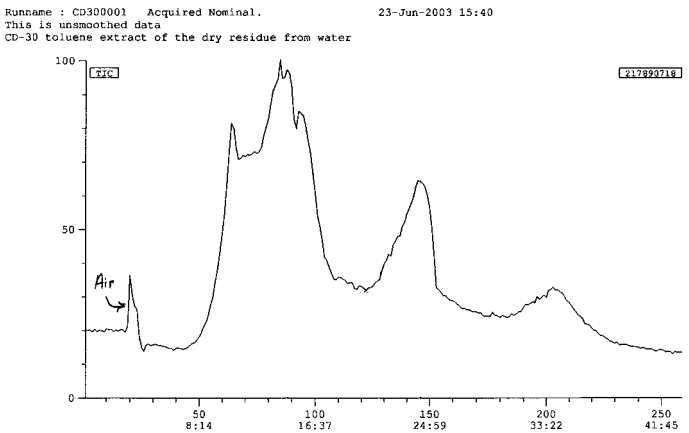


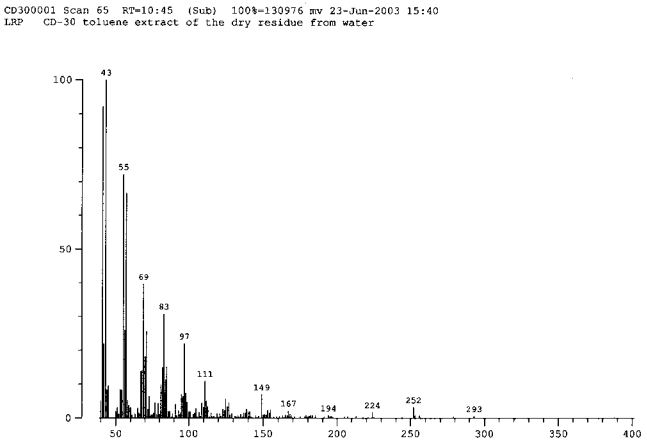
Figure A5. FTIR of the residue from the toluene extracted aqueous dried residue of the CTPB propellant.

	Index	Match	Compound Name	Library Name
1	1148	88.30	EM-350	Industrial Coatings
2	352	88.13	Dimethylpolysiloxane; General Electric SF96-1000, n=1,000 ct	Sprouse Polymers by Transmission
3	1115	87.51	DREWPLUS L-418	Industrial Coatings
4	225	87.48	Poly(dimethylsiloxane) (n=60,000)	Sprouse Polymers by Transmission
5	1046	87.11	ANTI-FOAM F-1	Industrial Coatings
6	1147	86.93	DC-347	Industrial Coatings
7	1146	86.43	EM-250 66%	Industrial Coatings
8	820	85.94	FOAMEX N	Industrial Coatings
9	880	85.32	Q1-8030	Industrial Coatings
10	160	84.09	P-C 165	Industrial Coatings

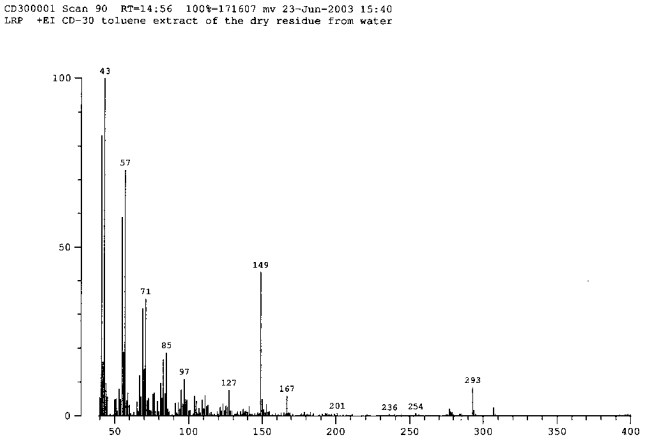
Figure A5a. List of literature search results.



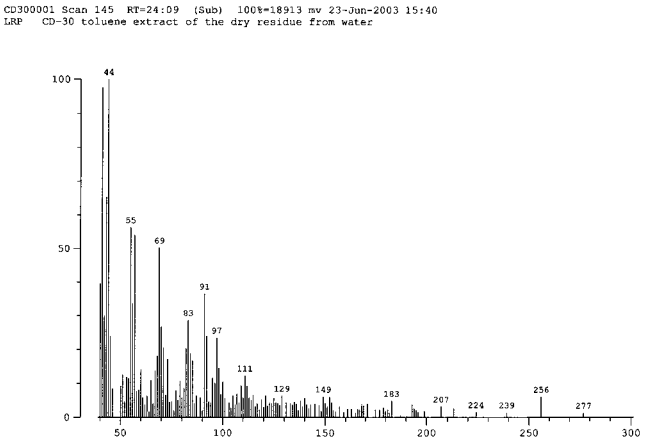
TIC



Scan 65



Scan 90



Scan 145

Figure A6. TIC of the SP-MS analysis of the residue from the toluene extracted aqueous dried residue from the CTPB propellant and mass spectra at scans 70, 90, and 100.

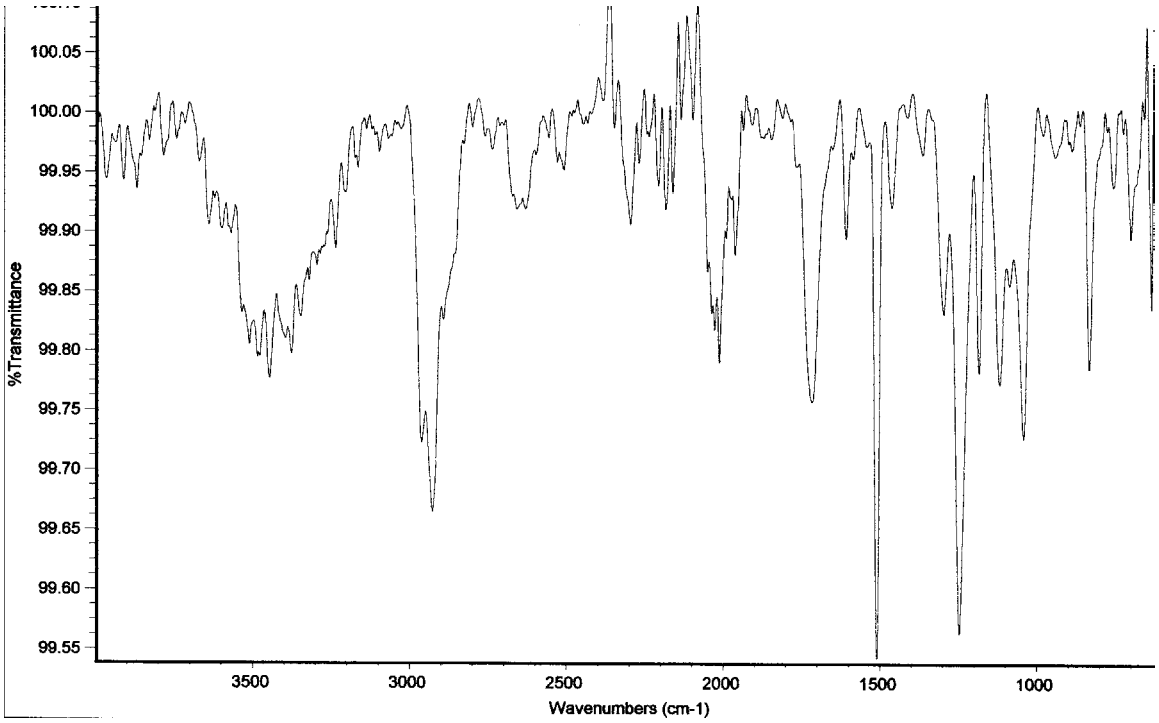
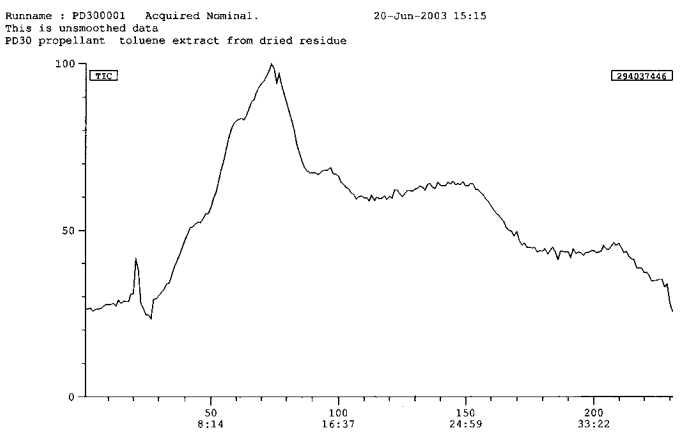


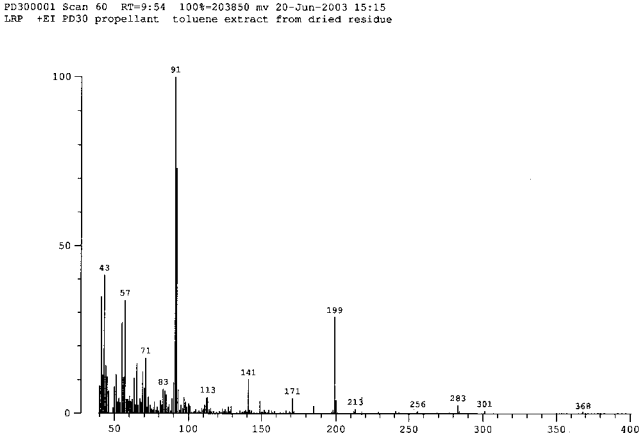
Figure A7. FTIR spectrum of the residue from the toluene extracted aqueous dried residue of the PBAN propellant.

	Index	Match	Compound Name	Library Name
1	843	85.37	DER 667	Industrial Coatings
2	1231	85.30	PXKH 6956	Industrial Coatings
3	866	85.04	CMD 35201	Industrial Coatings
4	929	85.03	EPON 1004F	Industrial Coatings
5	358	84.85	EPI-REZ 520 C	Industrial Coatings
6	1082	84.77	PXKS 6978	Industrial Coatings
7	8	84.11	EPON 1002 ADD MELT HFM 2JUN80	POLYMER ADDATIVE DERESOLED LIB.
8	946	84.06	EPON 1001-HX-75	Industrial Coatings
9	1641	83.94	UCAR PKHH	Industrial Coatings
10	32	83.91	Phenoxy resin (nom mw: 28,000)	Sprouse Polymers by Transmission

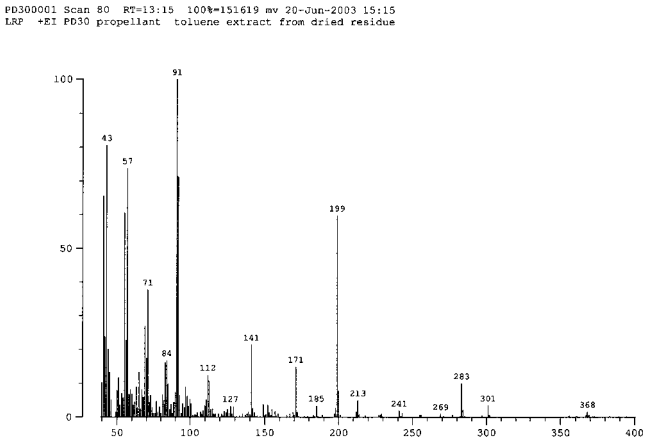
Figure A7a. List of literature search results.



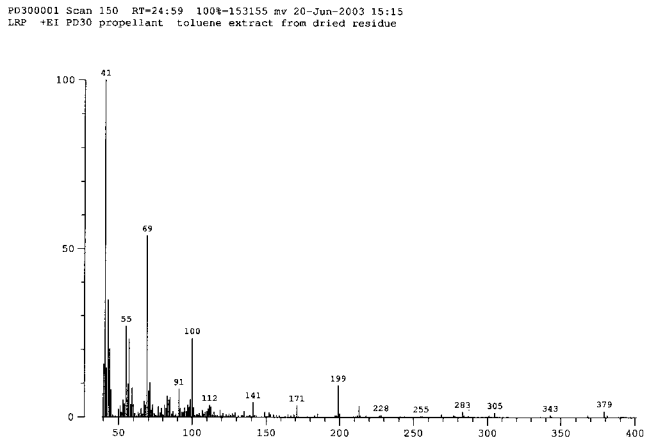
TIC



Scan 60

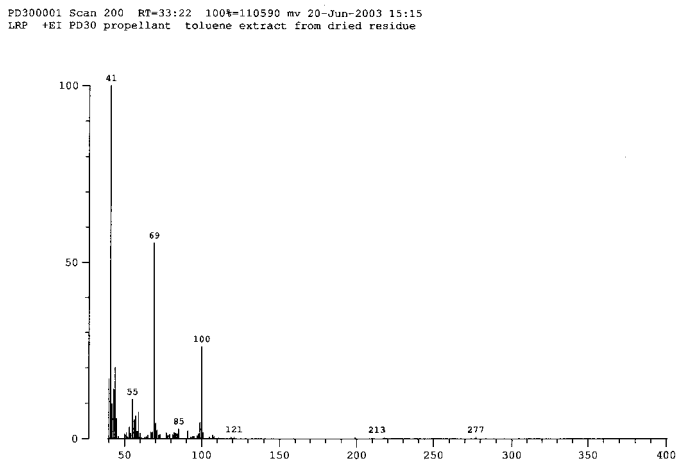


Scan 80

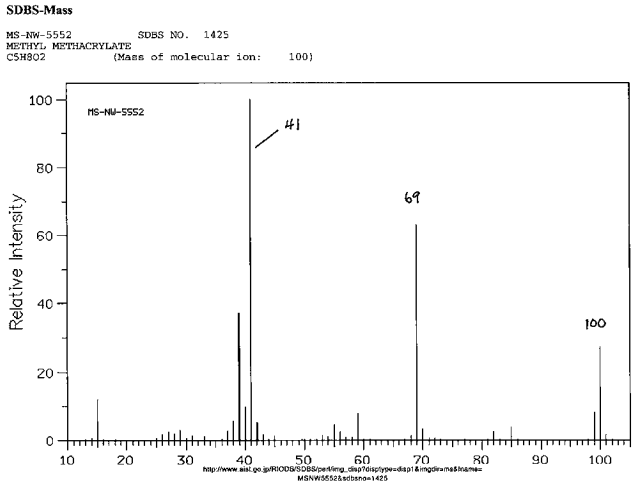


Scan 150

Figure A8. TIC of the SP-MS analysis of the residue from the toluene extracted aqueous dried residue from the PBAN propellant and mass spectra at scans 70, 90, and 100.



Scan 200



MMC

Figure A8 (continued). Mass Spectra of scan 200 and standard methyl methacrylate from SDBS library.

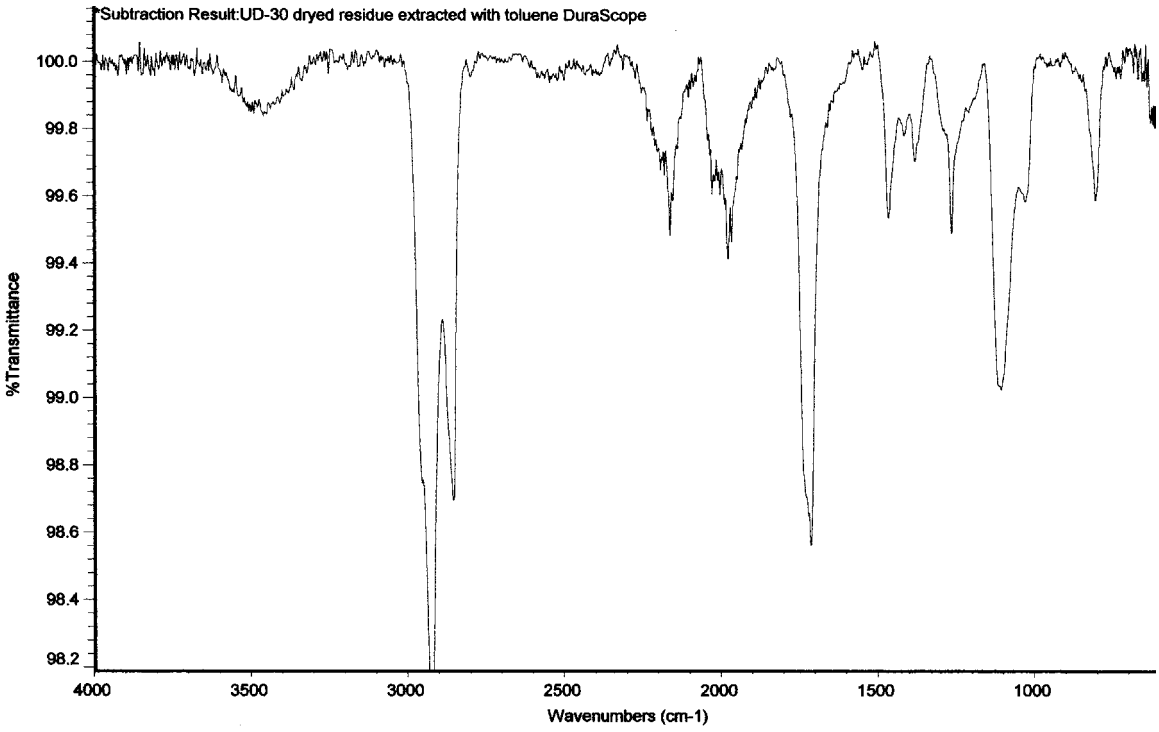


Figure A9. FTIR spectrum of the residue from the toluene extracted aqueous dried residue of the PU propellant.

	Index	Match	Compound Name	Library Name
1	1665	77.08	Enamel,Acrylic	Georgia State Forensic Automobile Paints
2	488	75.31	Propylene glycol ricinoleate	Sprouse Polymers by Transmission
3	483	74.18	Butyl ricinoleate	Sprouse Polymers by Transmission
4	1298	73.72	L-198	Industrial Coatings
5	1645	72.78	THERMOLITE 831	Industrial Coatings
6	624	72.66	SYLVATAC 315	Industrial Coatings
7	524	72.63	PRINT CONCENTRATE 430 M	Industrial Coatings
8	1299	72.46	NALCO 2321	Industrial Coatings
9	572	72.20	BALAB 3056A	Industrial Coatings
10	1033	72.13	COLLOID 711	Industrial Coatings

Figure A9a. List of library search results.

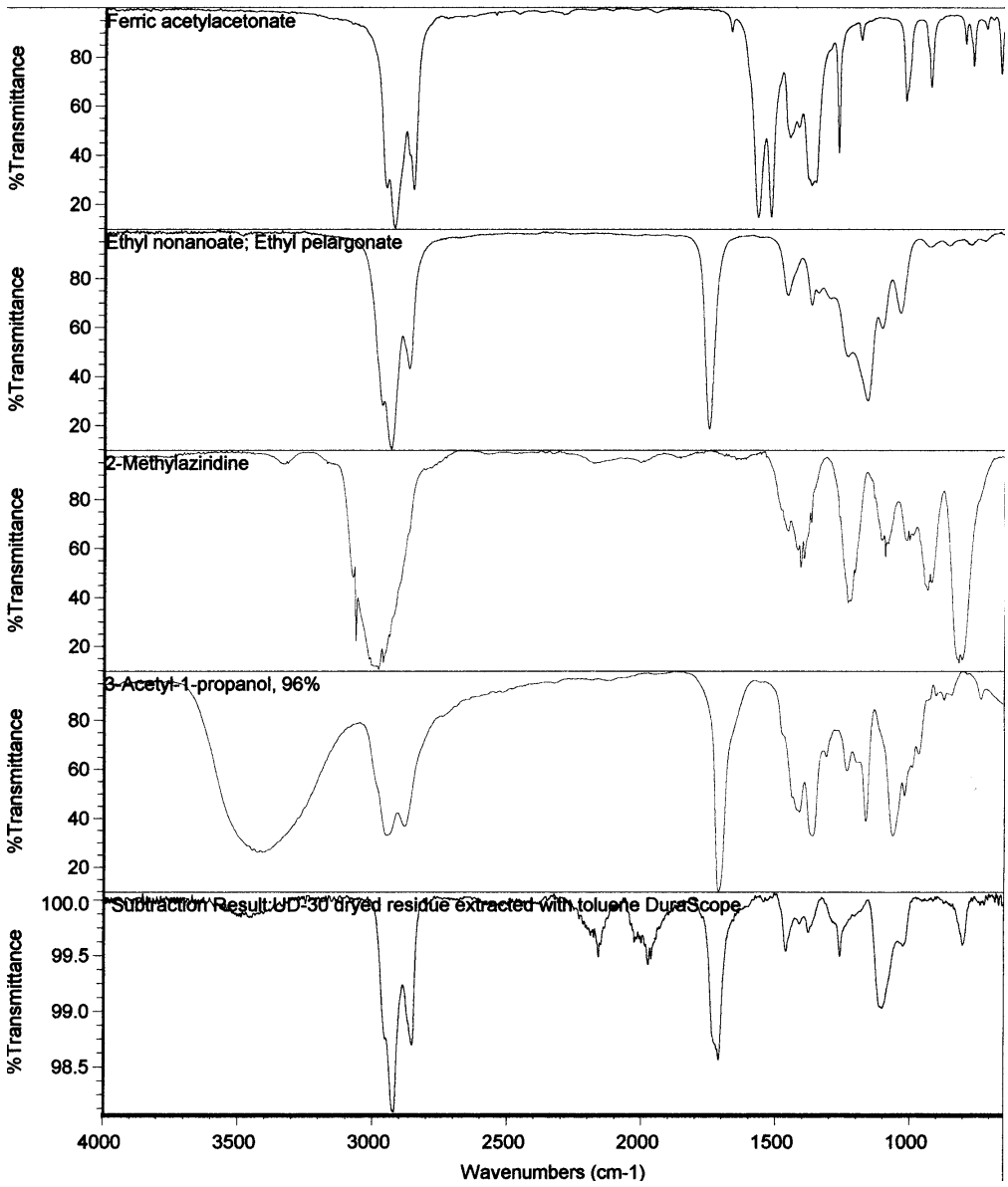
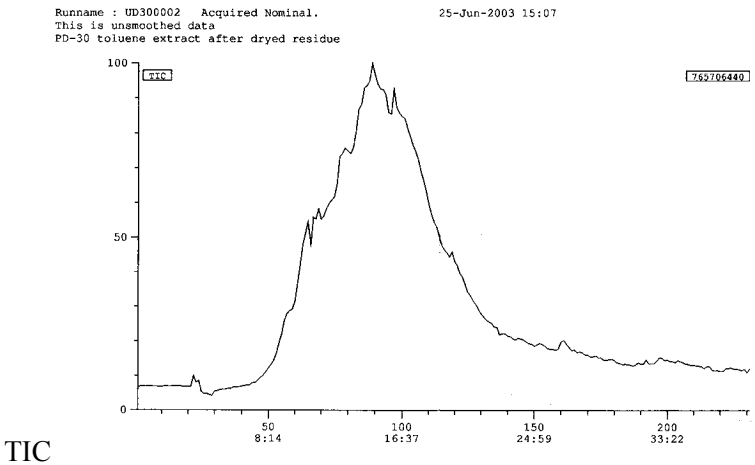
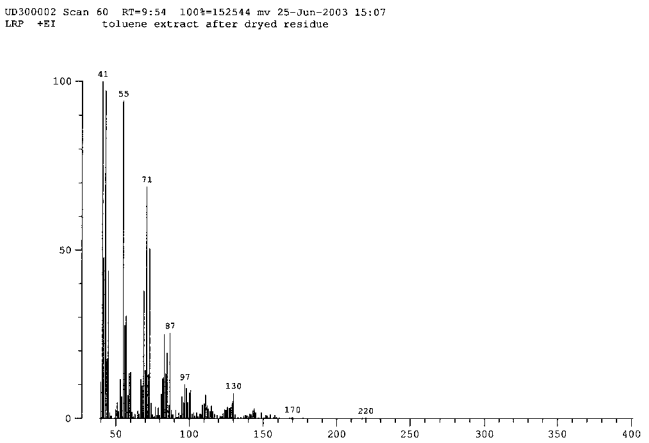


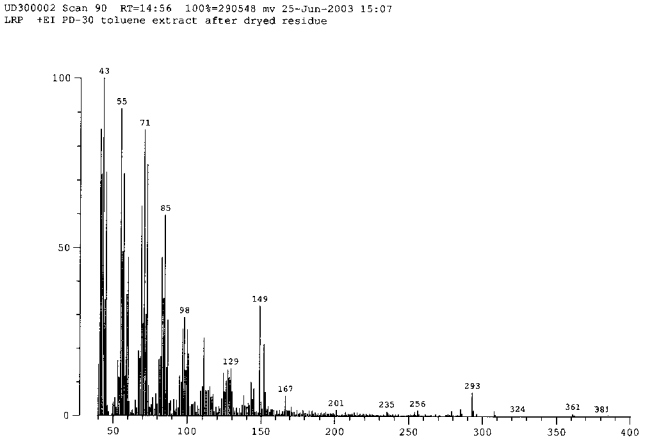
Figure A10. FTIR spectra of FeAA, ethyl pelargonate, methyl aziridine, 3-acetyl-1-propanol, and the residue from the toluene extracted aqueous dried residue from PU propellant.



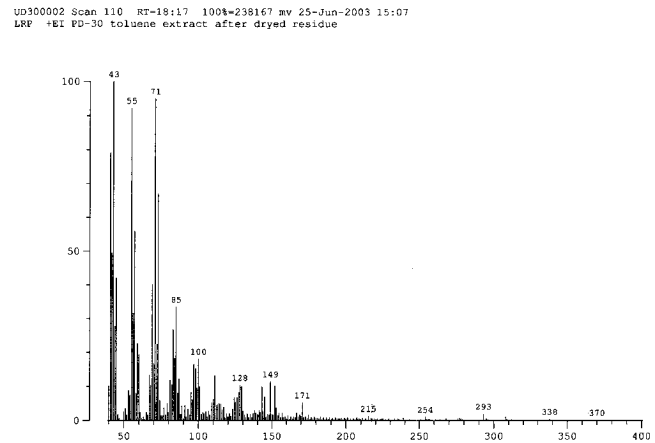
TIC



Scan 60

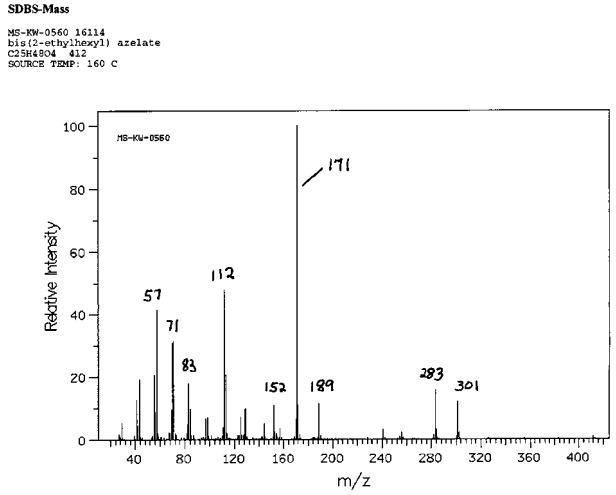


Scan 90

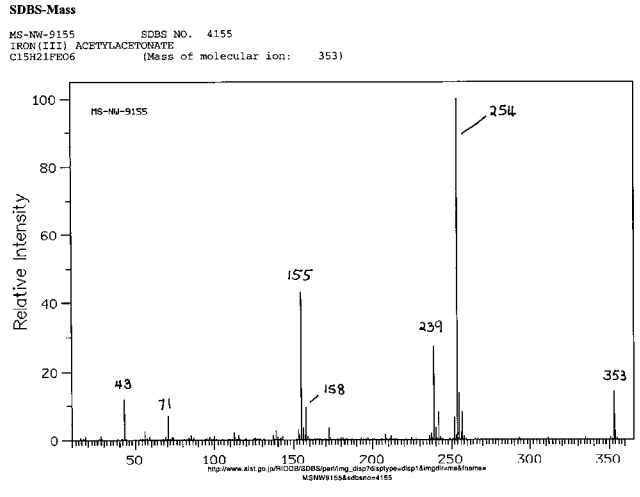


Scan 110

Figure A11. TIC of the SP-MS analysis of the residue from the toluene extracted aqueous dried residue from the PU propellant and mass spectra at scans 70, 90, and 110.



DOZ



FeAA

Figure A11a. Mass spectra of standard DOZ and FeAA.

A5. Summary

The water-extractable materials from four solid propellants that were immersed for 11 months were identified by inductively coupled plasma mass spectrometry (ICP-MS), Fourier transform infrared spectroscopy (FTIR) and solid-probe mass spectrometry (SP-MS). The four propellants were representative of the main types of binder—HTPB (hydroxyl terminated butadiene), CTPB (carboxy terminated butadiene), PBAN (poly butadiene acrylic acid acrylonitrile) and PU (poly urethane)—used for manufacturing solid propellants. The total residue from the aqueous solutions corresponded to the % of AP in the propellant formulation since the main extractable material was ammonium perchlorate (AP), the oxidizer.

Aluminum (Al), the fuel, was found in the aqueous solution from all the propellants, however, at a significantly lower concentration (i.e., about 1000 times lower) than expected from the relative amount of the AP leached out from the propellant. The iron oxide (Fe_2O_3) was not detected in the solutions from the PBAN propellant. It appears that the binder traps the aluminum and the iron oxide. Iron from the ferric acetyl acetonate (FeAA) was detected in the aqueous solution of the PU propellant by ICP-MS as well as by SP-MS. The FTIR analysis also indicated the possibility of the presence of the possible hydrolysis product, 4-hydroxy-2-pentanal.

The triphenyl bismuth (TPB) was identified in the aqueous solution of the HTPB by all techniques. The FTIR and the SP-MS identified triphenylphosphine oxide (TPO) as a possible extracted material. This material was unexpected, and the only possible source is to be an impurity in a propellant ingredient.

No silicon was found in the aqueous solutions of the PU propellant that contained silicone oil. Propylene glycol (PPG) was the only binder material identified from the FTIR spectrum in the residue of the toluene extraction of the dried aqueous residue from the PU propellant. The curatives for PU propellant were not detected by FTIR or SP-MS. The plasticizers dioctyl azelate (DOZ) and isodecyl pelargonate (IDP) are also possible extracted materials from the PU propellant.

The presence of AP in the residue from the propellants' aqueous solutions complicates the analysis for the organic residues. Toluene, a good solvent for organic materials, was used for the extraction. The total amount of organic residue from the propellants was determined to be 1 to 4 micrograms per gram of propellant per liter.

Not all of the extracted materials detected by SP-MS and the FTIR were identified.

Attachment 1

June 12, 2003

Aerospace Corp
PO Box 92957
Los Angeles, CA 90009-2957

Attn: Myriam Easton / Mail Stop:M2-250

Job No: 64500 JO

LABORATORY REPORT

Samples Received: Five (5) Samples
Date Received: 05/30/2003
Purchase Order No: 4500103808

The samples were analyzed as follows:

D.J. Northington, Ph.D.
Quality Assurance Officer

Charles Jacks, Ph.D.
Senior Staff Chemist

9240 Santa Fe Springs Road • Santa Fe Springs, CA 90670 • Tel: 562.948.2225 Fax: 562.948.5850 • wcas.com

WEST COAST ANALYTICAL SERVICE, INC.

Aerospace Corp
Attn: Myriam Easton

Job No: 64500
June 12, 2003

Selected Metals by SOP 7040, Rev 8
Quantitative Analysis Report
Inductively Coupled Plasma-Mass Spectrometry

Parts Per Million (mg/L)

Sample ID	Aluminum	Bismuth	Iron
BD-30	0.0061	0.00009	ND
CD-30	0.083	0.00004	ND
HD-30	1.23	0.00061	ND
PD-30	0.034	ND	ND
UD-30	2.1	ND	0.11
Detection Limit:	0.002	0.00002	0.05

Date Analyzed: 06-05-03

Quality Control Summary

Sample: UD-30

Analyte	Sample Result	Duplicate Result	Average Result	Sample RPD	Spike Conc	Spike Result	Spike % Rec
Aluminum	2.10	2.12	2.11	0.9	0.1	2.19	NR
Bismuth	ND	ND	ND	NA	0.1	0.089	89
Iron	0.109	0.104	0.1065	NA	10	10.4	103

NR - Not reported; sample result is greater than spike concentration.
Date Analyzed: 06-05-03

Client: AEROSPACE CORP
Job Number: 66138

Silicon by SOP 7040, Rev 8
Quantitative Analysis Report
Inductively Coupled Plasma-Mass Spectrometry

Parts Per Million (mg/L)

Sample ID	Silicon
BD-30	1.1
CD-30	ND
HD-30	ND
PD-30	ND
UD-30	ND
Detection Limit:	0.1

Date Analyzed: 06-05-03

Quality Control Summary

Sample: T143 (Standard Refcrence Material)

Analyte	Sample Result	Certified Value	% Error LImit	% Error
Silicon	11.7	10.94	15	6.9

Date Analyzed: 06-05-03

Attachment 2

Sample	% ClO4- in propellant	% Al in propellant	% TPBi in propellant	% FeO in propellant	Al/AP factor	TPBi/AP factor	Fe/AP factor	ClO4- conc. mg/L	Calc conc Al mg/L	Calc conc Bi mg/L	Calc conc Fe mg/L
HD-30	69	19	0.01		0.2754	0.0001		2995	824.71	0.43	
CD-30	73	15			0.2055			2487	511.03		
PD-30	69.78	16		0.22	0.2293		0.0032	3395	778.45		10.70
UD_30	65.37	17		0.04	0.2601		0.0006	4451	1157.52		2.72

LABORATORY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Laboratory Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual organizations:

Electronics and Photonics Laboratory: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, data storage and display technologies; lasers and electro-optics, solid-state laser design, micro-optics, optical communications, and fiber-optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Space Materials Laboratory: Evaluation and characterizations of new materials and processing techniques: metals, alloys, ceramics, polymers, thin films, and composites; development of advanced deposition processes; nondestructive evaluation, component failure analysis and reliability; structural mechanics, fracture mechanics, and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle fluid mechanics, heat transfer and flight dynamics; aerothermodynamics; chemical and electric propulsion; environmental chemistry; combustion processes; space environment effects on materials, hardening and vulnerability assessment; contamination, thermal and structural control; lubrication and surface phenomena. Microelectromechanical systems (MEMS) for space applications; laser micromachining; laser-surface physical and chemical interactions; micropropulsion; micro- and nanosatellite mission analysis; intelligent microinstruments for monitoring space and launch system environments.

Space Science Applications Laboratory: Magnetospheric, auroral and cosmic-ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; infrared surveillance, imaging and remote sensing; multispectral and hyperspectral sensor development; data analysis and algorithm development; applications of multispectral and hyperspectral imagery to defense, civil space, commercial, and environmental missions; effects of solar activity, magnetic storms and nuclear explosions on the Earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation, design, fabrication and test; environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions, and radiative signatures of missile plumes.